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THE THEORETICAL PRINCIPLES
OF THE
METHODS OF ANALYTICAL CHEMISTRY
BASED UPON
CHEMICAL REACTIONS

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Theoretical Principles

OF THE

Methods of Analytical Chemistry

Based Upon Chemical Reactions

BY

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à l'école nationale des Mines

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April, 1909.

A. T. L.
D. H. C.

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THEORETICAL PRINCIPLES OF THE METHODS OF ANALYTICAL CHEMISTRY BASED UPON CHEMICAL REACTIONS

INTRODUCTION

ANALYTICAL chemistry, freed from the traditional empiricism of the metallurgists in the eighteenth century through the genius of Bergman and Lavoisier, was placed upon a definite basis in the nineteenth century by Gay-Lussac and Berzelius. It then became the indispensable tool which permitted the discovery of the chemical laws of mass and of volume governing the proportions in which simple bodies combine in order to form definite compounds. The history of the beginning of analytical chemistry is thus intimately connected with the early development of general chemistry.* After Berzelius, however, had brought a definite system into the operations of analytical chemistry, this subject seems to have been considered a definitely closed chapter of general chemistry. The connection between the two has diminished little by little until analytical chemistry is regarded in general as an art (essentially practical) rather than as a science in which the speculations of theory can find a place.

Rivot, Fresenius, H. Rose, the immediate followers in the work of Berzelius, seem to abstain intentionally in their treatises from applying the methods which they advocate to the conceptions of general chemistry. They all limit themselves to the exact presentation of the details of manipulation, which are only essential in obtaining accurate results through their value as directions for carrying out the operation and have no visible connection with the general laws of chemistry.

H. Sainte-Claire Deville† tried, it is true, as early as 1853, to counteract the prejudice of analysts against any purely scientific

* G. Chesnau, *l'Evolution de l'Analyse minérale* (*Revue scientifique Series* (5), iii, 321 and 357 (1905) Paris).

† Saint-Claire Deville, Am. Chim. Phys. (3) xxxviii, 5 (1853).

discussion by showing in an article, highly important in the history of analytical chemistry, in what manner the systematic study of the stability of a class of salts, the nitrates, subjected to the action of heat, permits the formulation of an irreproachable method of separation of the alkaline earth elements from the sesquioxide of iron and aluminium.

This example was practically the only one of its kind for a long time, and it is only in recent years that, for the first time, one of the masters of modern theoretical chemistry, W. Ostwald, has undertaken, in a work which has quickly become classic in Germany,* to subject the methods of analytical chemistry to the recently established laws of equilibrium.

Most of these methods are, in reality, based upon the fact that the decomposition of salts gives rise to the phenomenon of equilibrium between two opposite states (the initial substances and the products of the reaction), as Berthollet had so accurately foreseen a century ago and which has been definitely established by the experiments of the Norwegian chemists, Guldberg and Waage, those of W. Ostwald and of several others, as well as by the thermochemical investigations of Thomsen and M. Berthelot. Van't Hoff and H. Le Chatelier, guided by the theoretical conceptions of H. Sainte-Claire Deville, have shown that the law which governs the double decomposition of salts may be deduced from the principle of thermodynamics applied to chemical equilibrium.

The reactions, utilized in an analysis, ought not then, in many cases, to be considered as absolutely complete, even when an insoluble precipitate is produced and the reaction may appear to run to an end. These new laws teach us that there may escape the notice of the analyst, deceived by the insolubility, appreciable quantities of the element which he is to determine from the weight of the precipitate obtained. Without doubt the work of Berzelius and of his successors has already brought about the empirical solution, in numerous cases, of the problem of causing the reaction to run to

* W. Ostwald, *Die wissenschaftlichen Grundlagen der analytischen Chemie, Leipzig,* 1894. A translation into French, by A. Hollard of the 3d German edition, has been published under the title of: *Les Principes scientifiques de la Chimie Analytique* (Paris, C. Naud, ed. 1903).

An English translation of the various German editions has been prepared by McGowen and published as *The Foundations of Analytical Chemistry* by The Macmillan Company, 3d edition, 1908.—*Editors' Note.*

practical completion in the desired direction. There is no doubt, however, but that the recent theories upon equilibrium, which alone allow one to understand the reason for the processes, will succeed in determining more definitely the conditions of their application.

The object which analytical chemistry is to pursue, then, is not only to increase the number of methods by extending the list of insoluble precipitates, but also, and especially, to increase the exactness of the methods already known, by investigating in the light of the recent physico-chemical theories the conditions which render the reactions as complete as possible. The moment seems to have arrived for analytical chemistry to enter this path under the stimulus of industrial demands which are endeavoring more and more to vary the qualities of the ordinary metals by the introduction of accurately proportioned infinitesimal quantities of foreign elements. The bond which unites analytical chemistry to general chemistry thus finds itself strengthened.

In my instruction in the School of Mines, I endeavored to apply these new theories to the critical examination of the processes of analytical chemistry, thus following the example of the illustrious leader of the German School of Physical Chemistry, but in advancing in this study, I have been led to adopt a method different from that which is advocated by that school. The fundamental principle of the theory of Ostwald, based upon the phenomena of Electrolysis, consists in attributing to salt solutions a hypothetical composition of elements, or groups of elements, termed "ions," which are the sole active agents in the double decomposition of salts. This purely electrolytic theory appeared to me in contradiction to a number of continually increasing facts, firmly established by experiment, and it seemed to me preferable in the discussion of the processes of analytical chemistry to employ a method, which I will call "Calorimetric," depending only on the calorific phenomena involved in the occurring reactions, and on the laws deduced from the principles of Thermodynamics.

My eminent colleague, Professor H. Le Chatelier, kindly permitted me to present these principles before the *College de France* in his chair of analytical chemistry, as substitute professor during the first semester 1904-1905. The work which I present here reproduces the lectures which I devoted to the methods based upon chemical reactions, properly speaking. I have omitted the parts of this course treating of methods based upon Electrolysis, Spectroscopy, Micro-

graphy, etc., the theories of which enter more especially into the domain of Physics and have been presented already in a number of excellent treatises.

Plan of the Work

The processes of analytical chemistry consist, in general, in bringing each element successively to the state of a definite compound in a final system, formed of distinct phases, whose nature lends itself easily to a separation by purely mechanical processes. Such systems can be obtained chemically from irreversible reactions such as phenomena of oxidation by dry or wet processes, of decomposition by heat, etc., or from reversible reactions by double decomposition, chosen from among those whose equilibria can be obtained in conformity with a practically complete reaction.

Since these two classes of reactions depend upon distinct principles, it is best to study successively the methods based upon each class. However, in the case, by far the most frequent, in which the final system is a precipitate formed in the presence of a liquid, the two kinds of methods necessitate the same discussion from the point of view of the conditions necessary to obtain the precipitate in the pure state. The plan of our study will be then the following:

In Chapter I, we shall examine the influence of the physical state of the precipitates (size of grains, crystalline state, colloidal state) upon their purification by washing.

In Chapter II, the theoretical principles involved in the methods based upon irreversible reactions will be studied and then these principles will be applied to some of the special methods chosen as types from among the most important of this class.

The study of the methods based upon reversible reactions by double decomposition of salts will be made afterwards, according to the same plan, but will be much more extensive on account of their great importance in analytical chemistry. Besides, it has appeared necessary to present the electrolytic theory, together with our calorimetric method, and to indicate the experimental evidence appearing to us in favor of the latter. Under these conditions, then, Chapter III will be devoted to the study of the principles involved according to the calorimetric theory, in reversible reactions, Chapter IV to the presentation of the electrolytic theory of these reactions, and Chapter V to a comparison of the two methods.

In Chapter VI we will formulate the theory of the general processes which produce complete precipitation, as far as possible, in double decomposition and, inversely, which cause precipitates insoluble in water to become soluble.

Finally in the last chapter, we shall apply the principles established in the preceding chapters to some particular methods based upon double decomposition.

We shall omit, in this study, all treatment of the deduction of the laws of chemical energy based upon the principles of Thermodynamics, merely citing special works or articles published upon this subject, and we will content ourselves with applying these laws to reactions employed in analytical chemistry.

CHAPTER I

INFLUENCE OF THE PHYSICAL STATE OF PRECIPITATES UPON THEIR PURIFICATION BY WASHING

1. Washing the Precipitates

THE most frequent operation in analytical chemistry consists in producing in a homogeneous liquid an insoluble precipitate, containing in the form of a definite compound one of the elements to be determined and to separate it from the mother liquor by filtration through a porous membrane whose pores are large enough to let the liquid pass and small enough to retain all the solid particles. In analytical chemistry we utilize, as filtering media, the Berzelius paper or asbestos and at times diminish the size of the pores by different artifices (such as covering with a gelatinous substance which plays the part of a material with pores still finer than those of the filter). The speed of the flow of the liquid may be accelerated by increasing the temperature, which diminishes the viscosity, and by diminishing the pressure under the filter.

The simple filtration of a mixture of a solid and a liquid does not give an exact separation because the solid remains moistened by the liquid and thus retains a certain amount of it by reason of the viscosity of the liquid and the attraction (capillarity) between the solid and the liquid. We assume that the quantity of the liquid thus retained by wetting is approximately proportional to the total surface of the grains, and it is easy then to calculate that for the same weight of solid substance, this quantity is roughly directly proportional to the fineness of the grains. This explains the fact that in the case of gelatinous bodies which represent the maximum of fineness of precipitates (grains invisible under the most powerful microscopes) the wetting liquid is practically continuous.*

* There have been issued very recently (1908) by the U. S. Department of Agriculture, Bureau of Soils, two Bulletins: No. 51 on the *Absorption of Vapors and Gases by Soils* by H. E. Patten and F. E. Gallagher, and No. 52 on *Absorption by Soils* by H. E. Patten and W. H. Waggaman. In the

The separation of the liquid and the solid forming the initial heterogeneous mixture can be complete only upon the condition of displacing the initial liquid by another liquid in which the solid particles are insoluble, while the original liquid is soluble in it; this result is accomplished by the operation of washing.

It should be easy to expel completely the liquid employed in washing by simple evaporation; the latter ought to be done in general at a temperature higher than the boiling-point of this liquid, for it is known that the tension of vapor moistening the surface of the solid is, on account of the capillarity, very much lower than that of the same liquid taken in mass.

Theoretically, if a precipitate had no physical action upon the soluble matter in solution in the mother liquor, a very limited number of washings would be sufficient to purify it completely. In this case, in fact, the volume v of the moistening liquid impregnating the filter and the precipitate is constant, and at each addition of the washing liquid, there is a uniform dilution in the volume V of the whole of the liquid; the substances in the moistening liquid are then brought at each addition to the fraction $\frac{v}{V}$ of the weight which they had after the draining of the preceding liquid, so that, after n additions of the washing liquid, the impurities are reduced to the fraction $\left(\frac{v}{V}\right)^n$ of their initial value. We thus see that the residue of impurities will be as much less as n is greater, and V greater in comparison with v. In order to diminish v, we start with a weight of precipitate as small as is allowed by the degree of precision of the balance compared to the degree of accuracy which we wish to obtain, and we take filters of small surface. By diminishing the latter, we reduce necessarily the volume of the wash liquid in a still greater proportion, which opposes the attainment of the desired result. Practically we proportion as much as possible the size of the filter to that of the volume of the precipitate in such a manner that v does not exceed about the tenth part of the total volume V of the liquid which the filter can contain. Starting with this, if we put $\frac{v}{V} = \frac{1}{10}$, we see that four washings will suffice in order to reduce

latter there is presented an excellent résumé of the work which has been done on the subject of absorption and they both contain a large amount of valuable experimental data.—*Editors' Note.*

the impurities retained by the filter and the precipitate to $\frac{1}{10000}$ of their initial value, which is quite sufficient in practical work.

Phenomena of Absorption and Adsorption.—Experiments prove, unfortunately, that, in most cases, the purification is much less than the preceding reasoning indicates, and that a much greater number of washings are necessary in order to obtain an acceptable degree of purity. By reason of an attraction which exists between the solid bodies and the bodies dissolved at the surface of contact, the liquid impregnating the precipitate and the filter retains a proportion of impurities greater than the liquid which is filtered, instead of having the same concentration in impurities, as we assume above. There is an *absorption* or *adsorption* of the dissolved impurities by the precipitate, so that the quantity of impurities remaining after each washing is greater than that which we have assumed, and the quantity carried away during each washing is smaller.

The phenomena of absorption were very accurately observed by H. Sainte-Claire Deville, in the paper previously mentioned (*loc. cit.*); "The wet analytical processes," he says, "are often attended by a source of error upon which the attention of chemists has not been sufficiently fixed until now, the phenomena of the *absorption* of the soluble substances by precipitates at the moment when they are forming. Each time that a solid body, in becoming separated in the midst of its solution, takes the form of a voluminous precipitate, it draws with it, in a proportion often quite large, a part of the various materials which are contained in the solution. This fact is well known in the case of ferric and aluminium hydroxides, when one wishes to separate them from calcium, magnesium, manganese, etc., and even from potassium. It is difficult to say in what state the precipitate and the absorbed material are found in relation to each other; but we can compare them to animal charcoal and to a coloring matter which, certainly, do not combine in the manner of very definite compounds. These are the facts which Chevreul attributes to capillary attraction."

We will see later in the chapter dealing with colloidal bodies, that many of the more recent works* have added little to the very exact views of H. Sainte-Claire Deville upon the absorption of dissolved substances by precipitates. The absorption is particularly marked in alkaline solutions, and to a less degree in acids and neutral

* A notable exception is the work of the Bureau of Soils, Bulletins 51 and 52, *loc. cit.*—*Editors' Note.*

salts; it is more manifest in proportion as the precipitates are finer, and it reaches its maximum in bodies of a gelatinous consistency. Filter paper itself has a very great absorbing power for alkaline solutions;—the following experiment cited by Ostwald (*loc. cit.*) is a striking example of this fact. A drop of a solution of barium hydroxide placed upon filter paper is freed from the alkaline substance which remains absorbed by the paper in the center of the circle formed by the liquid while nothing but pure water passed towards the outside. It suffices in order to verify this, to inclose with a pencil mark the moistened disc when the drop has stopped spreading out and to moisten the paper with phenolphthalene which alkalies color pink; the center alone of the disc shows the coloration characteristic of alkalies.

It results from these phenomena of absorption that, if one has to determine from a definite fraction of a volume of liquid, a substance dissolved therein, and if he has previously to separate a precipitate in suspension by filtration, it is necessary to reject the first portions of the filtrate because they are weaker in the dissolved substances through the absorbing influence of the filter. The latter attains very quickly its state of equilibrium, and the filtrate at the end of a few minutes is of the same concentration as the solution poured upon the filter.

For the same reason, if the solid body has a considerable absorptive power for the dissolved substance, and if it is a question of determining this constituent in an aliquot part of the liquor, one ought, owing to the danger of obtaining low results, to bring in suspension, by shaking, all of the precipitate immediately before taking a sample of the liquid. This is a precaution which, for example, it is necessary to observe in the chlorometric test for chloride of lime, which, in aqueous solutions gives an abundant residue of solid calcium hydroxide, and this has a considerable absorptive power for hypochlorite of calcium in solution.

By reason of these phenomena, no other practical rule can be given, in general, for the greatest possible purification of a precipitate than to repeat the washings as long as one can detect in the filtrate by suitable reagents the impurity which is to be eliminated.

All that we have said about filtration is applicable to washing by decantation, based upon the same principle as filtration, but less rapid because the residue of impurities, left after each washing, has, in general, a much greater relative value than in filtering, and

because it is necessary to renew the wash liquid a much greater number of times than in filtering to arrive at the same degree of purity. The use of centrifugal machines, permitting the accumulation of the precipitate at the bottom of the decanting jars and the decantation each time of almost the total quantity of the liquid, permits, in some cases, of complete washing by decantation.

2. Increase in the Size of the Grains of Crystalline Precipitates

In consequence of the preceding considerations, it is advantageous in filtering, that the grains of the precipitate should be sufficiently large, and, if they are of colloidal consistency, that they should be the least gelatinous possible.

It has long been known experimentally, that one can succeed in increasing very considerably the size of the grains by allowing the precipitate to remain in the same liquid in which it was produced, preferably hot. There results, if the precipitate is of a crystalline nature, a disappearance of the smallest crystals, and a growth of the largest crystals; the higher the temperature the more rapid the growth. It is for this reason that certain precipitates, too fine to be filtered at the time of their formation,—as barium sulphate, calcium oxalate, which pass through the filter when they have just been precipitated,—are easily filtered after digestion, more or less prolonged in the warm mother liquor. For bodies precipitated in the amorphous gelatinous state, there is a general tendency under the same conditions, toward the production of denser flakes which are much more readily filtered.

It is only in recent years that the causes have been elucidated as a result of which the size of the grains of insoluble bodies increases by digestion in the mother liquor, namely: first, the influence of the fineness of the grains upon the solubility; second, the effect of the surface tension existing at the boundary between the liquid and the solid grains. We will study them successively, paying special attention to the first, which makes itself felt the more rapidly and is, consequently, the more important in analytical chemistry.

Influence of the Fineness of the Grains upon the Solubility.— Recent experiments of Ostwald, confirmed by those of Hulett, have demonstrated that the solubility of a solid body in a solvent, depends not only upon the temperature, but is also proportional to the dimensions of the solid particles which are in contact with the solution,

and is greater for extremely fine particles than for grains exceeding a definite size.

The discovery of these phenomena originated in the comparative study of the red and yellow oxides of mercury, carried on with a view of determining whether these oxides are dimorphous like the iodides, or not. Ostwald, having verified the fact that the cell

Mercury	Red Oxide of Mercury dissolved in Potassium Hydroxide	Yellow Oxide of Mercury dissolved in Potassium Hydroxide	Mercury

gives rise only to an imperceptible electromotive force, concluded* that the two varieties of oxides of mercury are identical, not only from the chemical point of view (as the calorimetric studies of R. Varet† leads one to believe, by showing that the transformation of one variety into the other produces no thermal effect) but also from the physical point of view, and differ only in the size of the particles.

These conclusions have been questioned by E. Cohen‡ who deduced from the small e. m. f. obtained by the above-mentioned cell sufficient evidence to prove the isomerism of the oxides of mercury and not their identity. Ostwald was led to think that the difference of potential produced by potassium hydroxide solutions of the two varieties of the oxide, was due to a difference of solubility, depending upon the fact that the yellow oxide is in finer grains than the red oxide. In order to demonstrate this, Ostwald§ referred to the reversible reaction:

$$2KBr + HgO + H_2O \leftrightarrow HgBr_2 + 2KOH,$$

in which about seven per cent of potassium bromide is transformed into potassium hydroxide, which is readily determined by testing for alkali. The normal solution of the bromide was placed with the oxide of mercury into glass flasks, which were placed in rotating drums, whose movement insured the saturation of

* W. Ostwald, *Zeit. phys. Chem.*, xvii, 183 (1895).
† R. Varet, *C. R.*, cxx, 622 (1895).
‡ E. Cohen, *Zeit. phys. Chem.*, xxxiv, 69 (1900).
§ W. Ostwald, *Zeit. phys. Chem.*, xvii, 427 (1895).

the solution with the oxide of mercury. By placing garnets into the flask one could pulverize very finely, by a prolonged rotation, the red oxide of mercury, whose color approached at the same time that of the yellow oxide. The following limits were thus obtained: The red oxide transformed 7.17 per cent of KBr into KOH, and the yellow oxide 7.68 per cent; this limit has reached 8.10 per cent with the red oxide, when mixed with garnets. This increase in comparison with yellow oxide depends without doubt upon the fact that the fineness of the grains is still greater with red oxide, thus triturated. It is a question, moreover, if this is a real equilibrium; for, in mixing red oxide with a solution saturated with yellow oxide, the limit is lowered from 7.68 per cent to 7.32 per cent, a limit very near 7.17, given by the red oxide, the difference arising from the fact that there is formed in this case fine powdered oxide, a precipitate from the supersaturated liquid, a circumstance which is not encountered in the reverse operation. In any case, the determination of the concentration, clearly shown in the presence of the larger grains of red oxide, removes all doubt of false equilibrium.

These experiments show, in an irrefutable manner, that the increase of fineness of the grains of red oxide of mercury by prolonged trituration increases its solubility in normal potassium bromide by about 13 per cent. With other substances but slightly soluble in water, Ostwald has obtained an increase in the solubility in the anticipated direction, although much less; 0.09 per cent with calcium oxalate, one per cent with lead chloride.

The views of Ostwald have been confirmed recently in a still more striking manner by the studies upon the solubility in water of gypsum and of barium sulphate, carried on by Hulett.*

The method employed consists in projecting the extremely finely pulverized salt into a solution saturated previously by long contact with large crystals of the same substance and in noting the electrical conductivity, which increases immediately, owing to the solution of the very fine particles supersaturating the liquid, then diminishes gradually, finally reaching the initial value at the end of a few days. By comparing the maximum conductivity thus obtained with grains of different sizes to that of solutions of known strength, the solubility corresponding to each size of grain can readily be determined. Hulett has thus obtained, at 25°, an increase in the solubility of 19

* G. Hulett, *Zeit. phys. Chem.*, xxxvii, 385 (1901).

per cent for gypsum referred to a normal saturated solution which contained 2.085 grams anhydrous $CaSO_4$ per liter, the solubility increasing to 2.476 grams with the pulverized gypsum. But observing the grains of the gypsum with a microscope provided with a micrometer, he has ascertained that the finest grains not increasing the solubility, have a size equal to 2 μ and that, in the finest powders increasing the solubility, there are no grains smaller that 0.2 μ, the average size being 0.3 μ. It is then the decrease in size from 2 μ to 0.3 μ which produces the increase of 19 per cent in the solubility.

With the sulphate of barium, the influence of the fineness of the grain on the solubility was still more pronounced; the salt precipitated on boiling, whose grains have an average size of 1.8 μ, gives the ordinary solubility of 0.00229 gram per liter; this precipitate pulverized as fine as possible (up to 0.1 μ) gives a solubility of 0.00415 gram and even up to 0.0046 upon shaking it with quartz powder. Finally, the pulverized natural sulphate, which furnished still finer grains, has given a solubility of 0.00618 gram per liter or an increase of 160 per cent referred to the standard saturated solution.

These experiments put beyond a doubt the increase of solubility with the fineness of the grain, starting with a certain limit of size, ϵ, depending upon the substance, but always of the order of size of the micron, μ, or the thousandth of a millimeter. The mechanism of this phenomenon, in apparent contradiction to the ordinary ideas upon the constancy of the coefficient of solubility of substances, may be conceived thus simply in the following manner.

The forces involved in the equilibrium of bodies in contact with their saturated solution (cohesion, surface tension, osmotic pressure), act only within extremely small distances, and make themselves perceptible consequently only within an extremely narrow zone at the surface of contact of the solid and the liquid. The same solution can then be in equilibrium with grains of different sizes provided that this size exceeds a certain definite limit, ϵ, and one has then the common phenomenon of *saturation,* independent of the size of the fragments of the solid body in contact with the saturated solution, and in relation with the external pressure and the temperature. But, if we introduce into the liquid thus saturated, a grain of smaller size than ϵ, the forces (cohesion), which in this grain produce equilibrium with the action of the liquid, have a smaller value than in the large fragments: the grain less than ϵ is no longer

then in equilibrium with the saturated solution, and we understand why it is dissolved. Then the liquid becomes *supersaturated* with respect to the fragments greater than ϵ, and the material dissolved from the small grains will deposit itself more or less quickly upon the fragments greater than ϵ.

If, then, all of the fragments of the solid are less than ϵ, the solution can reach a degree of concentration greater than the usual solubility coefficient,—without there being need of assuming two different states of hydration of the salt, as for sodium sulphate,—and it will be supersaturated; if on the contrary, there are some fragments larger, others smaller than ϵ, these latter will disappear by being dissolved, and their material will go to increase the larger ones, until all the grains have dimensions equal to or greater than ϵ.

The first of these two conditions is that which is to be realized in the case where certain anhydrous precipitates do not form immediately, notwithstanding their almost complete insolubility; the insoluble body is produced at the very first in grains much finer than ϵ and it remains in the supersaturated solution. It is only at the moment when this instable equilibrium is destroyed by any cause whatever, the elevation of temperature, the evaporation to dryness of the liquid at the circumference of the surface, etc., that the precipitate begins to appear and then separates rapidly. Such is the case of the sulphuric acid which one wishes to precipitate from solution by a very dilute solution of barium chloride. The solution often remains perfectly clear for a very long time, after which the precipitate suddenly appears. It is the same in the case of sulphur produced by the decomposition of sodium thiosulphate by hydrochloric acid, and which gives an unstable yellow solution which suddenly changes after some time, depending upon the concentration and the temperature, into fine precipitated sulphur.

It is the second condition (some grains larger, others smaller than ϵ) which is realized most often in the formation of very fine precipitates, barium sulphate, calcium oxalate, etc., obtained in liquids of medium concentration; by letting the precipitate remain for a long time in the mother liquor, the grains less than ϵ are allowed time to redissolve and to enlarge the grains greater than ϵ, this increase in the size of the largest grains being much more rapid with increase in the temperature by reason of the greater rate of diffusion of the dissolved molecules in the warm than in the cold solutions.

It is probably in a phenomenon of the same order that one must seek the explanation of the much easier and more rapid attack by acids and even by water of the silicates, of tungsten by aqua regia, of iron chromate by melted peroxide of sodium, etc., when these bodies are reduced to an extremely fine powder by grinding in an agate mortar and then passing through a silk sieve. The chemical action of water upon alkali-lead silicates (employed as translucent enamels upon gold or copper), according to the size of the fragment, gives in fact, as has been suggested, phenomena in every respect comparable to the increase of solubility by the fineness of the grain. Enamel in large grains can be preserved for years under water without undergoing any perceptible decomposition; if we crush it fine, and suspend it in water, the finest grains are instantly decomposed by the water, which takes from them a part of the alkali and renders them opaque, while the largest grains remain translucent and unchanged. The phenomenon is particularly clear in the case of very dark enamels (blue enamels, colored blue by the oxides of cobalt, for example), where after shaking and allowing to settle, we see the grains arrange themselves into two very distinct layers: at the bottom, the largest grains, unchanged, of dark color; above, a white deposit formed by the finest grains, decomposed by water and devitrified.* The microscopic examination of the powder of enamels thus preserved under water for several years has shown that the finest grains remaining unchanged by the water have a dimension of $\geq 2\mu$.

Influence of Surface Tension upon the Increase of Size in the Grains.—The second cause which tends to make the more voluminous grains increase at the expense of the smaller, even after the supersaturation, due to the fineness of the grains, has been destroyed, is the surface tension which must exist at the surface of separation between the precipitate and the mother liquor,—even without any solvent action involved,—similar to the one we perceive at the separating surface of two non-miscible liquids and which produces the phenomenon of capillarity. This surface tension tends to diminish as much as possible the total of the existing surfaces, so as to

* This phenomenon of *devitrification* is well known by the enamel manufacturers of Limoges. The workers attribute it to the action of crushing alone, an inexact explanation, for the finest grains crushed dry remain translucent, and it is the chemical action of the water alone which produces this effect, a result not given by benzine, petroleum, etc.

make the same volume of the body occupy the smallest possible surface.

This phenomenon can be shown more easily with liquids than with precipitates by shaking violently two non-miscible liquids in a flask: the emulsion of fine little drops of homogeneous appearance, thus produced, is finally resolved into two distinct layers or at least into large drops clearly separated. This is a well-known phenomenon for mixtures of water and oil, of water and mercury; in this phenomenon one can also employ the difference of density as aiding in this separation, but we produce it just as well with an emulsion of water and of aniline, which have practically the same density and which give, after standing, large drops of aniline floating at different depths in the water.*

It is this contact-tension of solids and liquids which explains the well-known enlargement of the large crystals at the expense of the little ones in the soluble salts in contact with a saturated solution. Gauss has given a mathematical theory of this phenomenon. P. Curie presents an elementary theory of it in a very interesting paper upon the formation of crystals and upon the capillary constants of their different faces;† the conclusions of this article alone will be indicated here.

If we consider several surfaces of separation S, S_1, S_2 . . . with capillary constants A, A_1, A_2 . . . limiting the body, the stable form will be the one which will give a minimum for the quantity $AS+A_1S_1+A_2S_2$ . . . If it is a question of a group of several crystals, each one of which possesses the most stable form, the group of crystals will have a minimum surface energy when their total surface will be the smallest possible, that is to say, when all the crystals will be united in one crystal.

An analogous tension must exist at the contact surface of chemical precipitates and their mother liquor; as these precipitates rep-

*Ostwald (*loc. cit.*) gives the following experiment to demonstrate the influence of the surface tension upon the diminution of surfaces of the same mass; two soap bubbles, one large and one small, are blown on the ends of two glass tubes which can be joined and the communication between the two bubbles can be cut off. The internal gas in each of the bubbles being in equilibrium with the external pressure, it seems that, if the two bubbles are put in communication, no change ought to be produced: it is not so at all, the smaller bubble diminishes in size and disappears, while the other becomes larger.

† P. Curie, *Bull. de la Soc. minéralogique de France,* viii, 145 (1885).

resent salt crystals of very slight solubility, but never of no solubility at all, there may be produced through the medium of the surrounding liquid continual exchanges among the solid particles, and the largest crystals increase more or less quickly at the expense of the smallest, even when the latter have a dimension greater than ϵ, just as in a crystallizing dish containing small alum crystals in contact with the mother liquor in which a large crystal has been suspended, the small crystals disappear little by little and the matter of which they are composed goes to increase the large crystal. One should also notice that, in the case of the precipitates called *insoluble* used in analytical chemistry, these phenomena occur with a much greater slowness than with the crystals of very soluble salts, and one never has to fear in practice that the crystals will increase to the extent of retaining some of the mother liquor mechanically included: so one should always leave the precipitates to digest as long as possible in their mother liquors, which should be preferably warm, to facilitate the exchanges between the small and the large grains.

3. Amorphous, Colloidal Precipitates and Pseudo-Solutions

A very great number of the precipitates utilized in analytical chemistry are obtained in a gelatinous amorphous form, such as the hydroxides of iron, aluminium, chromium, nickel, etc., most of the metallic sulphides, silica, fluosilicate of potassium, etc. The phenomena of absorption are here manifested with a particular energy, and their purification by washing is consequently very difficult, since they easily obstruct the pores of the filters and their filtration is very slow.

But this slowness, which would not be an insurmountable obstacle in their purification, is not the only drawback which these bodies present in chemical analysis. In the first place, in certain cases, the absorption of the soluble matter of the mother liquor by the gelatinous precipitate is so energetic that, however prolonged the washing with pure water, we cannot eliminate the last traces of the impurities which appear to form with the precipitate a solid solution or even a combination insoluble in water. Such is, for example, the case of the hydroxide of nickel precipitated by potassium hydroxide, which always retains a small trace (few per cent) of the alkali, manganese sulphide precipitated by alkali sulphide in the presence

of calcium salts, manganese oxide precipitated by bromine in the presence of potassium hydroxide, which retains a considerable proportion of the alkali, etc.

In the second place, these gelatinous precipitates have, almost all of them, the property of forming with pure water, a solution intermediate between solutions properly called, which are formed by soluble crystallized bodies, such as sea salt, or cane sugar, and the turbid mixtures formed by the suspension of very fine particles of insoluble bodies in water. These particular solutions of gelatinous bodies, which are called *pseudo-solutions or colloidal solutions** pass through all filters; they are often unstable but in many cases frequently met with in inorganic chemistry—these gelatinous bodies remain indefinitely in suspension. The types of these pseudo-solutions of inorganic gelatinous bodies are the solutions of the metallic hydroxides obtained by Graham by means of the dialysis of the inorganic salts in dilute solutions.

These colloidal solutions are destroyed, as we shall see, by the presence of acids and mineral salts which precipitate the gelatinous matter in the form of flakes, making it no longer capable of passing through the filter. Consequently when these colloidal bodies are produced in chemical analysis, they are coagulated in the form of flakes in the mother liquor on account of the presence of the dissolved inorganic salts coming from the reagents employed, and, when the whole is thrown upon the filter, the liquid passes clear. But, as soon as we begin to wash with pure water, the precipitating action of the inorganic salts decreases more and more, and the precipitate soon forms with the pure water a pseudo-solution which passes through the filter. This pseudo-solution, falling into the clear filtrate, precipitates again and gives the impression at that moment that the precipitate *passed through* the filler in the state of solid particles when it has really done so in the state of colloidal solution. From the practical point of view of washing, the result is, moreover, the same; it is impossible to continue the washings with pure water without danger of losing in the filtrate all or part of the precipitate, (case of colloidal ZnS, NiS, etc.).

It is only in quite rare cases in chemical analysis that colloidal bodies are formed in the absence of all saline matter, and conse-

* In the recent works upon colloidal bodies and colloidal solutions the former are designated also by the name, *hydrogels,* and the latter by the name, *hydrosols.*

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quently would remain in the original as pseudo-solutions. A well-known example is that of the cold solution of arsenious acid in pure water, which, treated with a small quantity of hydrogen sulphide, gives a yellow solution, passing through the filters and remaining a long time without change; a few drops of hydrochloric acid produce the precipitation of the sulphide of arsenic, which loses at the same time the property of again forming pseudo-solutions with pure water. The dilute solutions of stannic and antimonious chlorides can likewise give with hydrogen sulphide colloidal solutions, but slightly colored, and existing for some minutes without a precipitate, in spite of the presence of free hydrochloric acid, and this peculiarity may easily deceive one as to the presence of these metals in qualitative determinations.

A knowledge, as exact as possible, of the conditions in which are formed the pseudo-solutions and of the processes which permit their destruction or prevent their formation, is then necessary in chemical analysis where colloidal precipitates predominate, on account of the frequent use of the hydroxides and sulphides of the metals.

From the physical point of view, the colloidal precipitates are formed of particles or *nuclei* incomparably finer than crystalline precipitates, while the dimensions of the finest grains which the latter give, are of the order of a thousandth of a millimeter, those of the grains which form the colloidal bodies are of an order a thousand times smaller, and consequently, invisible under the microscope by the processes of ordinary observation. These particles can, however, be brought into evidence by a method derived from the well-known fact that the dust particles of the air, strongly illuminated by a ray of sunlight passing through a dark room, appear luminous and become perceptible to the naked eye; likewise, any object, however small it may be, becomes visible under the microscope, if it is lighted strongly by a very powerful ray of light, perpendicular to the optical axis and incapable of penetrating the apparatus. Thanks to this method, due to the German physicists Siedentopf and Zsigmondy, it has been possible to show the presence of particles of gold contained in the state of solid colloidal solution in pink Bohemian glass, as well as the nuclei of the colloidal solutions of copper ferrocyanide in water and bromide of silver in gelatine (Cotton and Mouton). By counting the particles appearing in a solution of given concentration, it has been possible to estimate their diameter at a few thousandths of a micron.

One can understand that, with such small dimensions, the surface energy can play a preponderant rôle in the forces involved in the contact of these particles and the liquids in which they are placed, and that the colloidal solution resulting from these actions may have very different properties from those of the ordinary solutions of crystalloidal bodies.

The *desiccation* of colloidal solutions or of colloidal precipitates, at ordinary temperature, produces different effects according to the bodies in pseudo-solution. Sometimes the residue is more or less granular with a dull and earthy fracture, and in that case, the matter, thus desiccated, is no longer capable of again forming a pseudo-solution by the addition of pure water; such are liquids made turbid by kaolin, silica, colloidal sulphides of arsenic, copper and mercury. At other times, on the contrary, the residue after desiccation furnishes an elastic body with brilliant and vitreous luster which, placed in contact with pure water, will again give a colloidal solution identical with the original pseudo-solution, such as gums, albuminoids, aniline dyes, etc. Colloidal substances are thus subdivided into *unstable* and *stable* colloids;* these latter allow indefinite re-solution in water like crystalloidal bodies, but with this difference,—that the stable colloids do not possess maximum coefficients of solubility at every temperature. There exist between the matter in the solid phase and its pseudo-solution intermediate *gummy* or *mucilaginous* conditions analogous to the plastic state in the solid amorphous substances such as glasses.

The stable colloids are most frequently organic substances and the unstable are inorganic (inorganic colloids, Ag, Pt, Ir, As_2S_3, SiO_2, etc.). There does not exist, however, any clearly defined separation in this respect between the organic and inorganic substances, certain colloidal hydrates of iron and chromium, even after prolonged desiccation can again form pseudo-solutions.

By taking the two extremes, the pseudo-solutions of gelatinous silica, clearly unstable, and the pseudo-solution of mastic, extremely stable, W. Spring† has shown the very clear difference of solidarity existing between the particles in both pseudo-solutions. By superposing a thick, turbid layer of mastic upon pure water in a test

* V. Henri and A. Mayer, *l'Etat actuel de nos connaissances sur les colloïdes* (*Revue général des sciences,* p. 1015 (1904)).

† W. Spring, *Sur la floculation des milieux troubles, Rev. des Trav. chimiques des Pays-Bas et de la Belgique,* xix, 204 (1900).

tube (the turbid mastic having a specific gravity of 1.0665), W. Spring has shown that the surface of separation, plane at first, takes little by little the spherical form, as if the upper layer had swollen uniformly; on the contrary, in a layer of silica superimposed upon pure water, the particles of silica descend parallel, and the surface of separation remains a plane. It is thus seen that turbid mixtures of silica finally precipitate at the end of a few weeks, while, for the mastic, time alone does not produce the clarification.

The *elevation of temperature* favors in certain cases, especially for the unstable colloids, the decomposition of the pseudo-solutions; such is the case of water clouded by clay in suspension, which, if the clay is very fine, remains turbid almost indefinitely and which becomes clarified according to C. Barus, about twenty times more quickly at 100° than at 15°. This clarification by elevation of the temperature can be obtained every time by prolonged digestion; heat modifies the precipitate by making it *granular* instead of gelatinous. Such is the case of aluminium precipitated by ammonium hydroxide, which, digested hot for some hours, becomes granular and is filtered more easily. Many metallic sulphides (MnS, ZnS, NiS, etc.), are much less colloidal when precipitated from boiling solutions; the flakes are then denser and filter better.

This transformation is still more rapid when the dried substance is heated, as in the case of *insoluble* silica obtained by heating the dried mass for some hours between 100° and 110°, which renders it not only insoluble in water, but also in very dilute acids. Finally a great number of gelatinous hydroxides of the metals, heated to a high temperature, are transformed into crystalline bodies with liberation of heat (ignited oxides), and lose definitely the faculty of forming pseudo-solutions; such are the oxides of iron, aluminium, chromium, etc. Once transformed thus into crystalloids whose grains are much larger than those of the original colloid, these oxides in general have no longer any appreciable power of absorption, and the inorganic salts introduced during the precipitation can then be easily removed if no chemical combination has been produced between the oxide and the elements of these salts during the heating. The hydroxides of nickel and of cobalt, even after ignition still retain strongly, however, the alkali absorbed during precipitation, and they must be reduced to the metallic state at a high temperature in a current of hydrogen, in order to be able to free

them of the alkali, for which the metallic conglomerate of crystalline granules has no longer any absorbing power.

This transformation by heat of colloidal precipitates, capable of forming pseudo-solutions, into crystalline bodies insoluble in water or weak acids, finds an interesting application in the quantitative determination of fluorine by the Berzelius method. The hydrofluoric acid is precipitated by calcium chloride in an ammoniacal solution containing an excess of ammonium carbonate, which gives gelatinous CaF_2, with an excess of $CaCO_3$. It is impossible to separate these two bodies by means of even a dilute acid solution because gelatinous CaF_2 forms pseudo-solutions with acidulated water, just as gelatinous silica. But, if we ignite the precipitate at low red heat, CaF_2 becomes crystalline and ceases to be soluble in acetic acid, while $CaCO_3$ is still soluble in it and washing by acetic acid permits one to obtain finally pure CaF_2.

Precipitation of Pseudo-Solutions by Salts.—All colloidal solutions and turbid liquids, in which the solvent is water, become clarified and allow the matter in pseudo-solution or in suspension to precipitate whatever may be its chemical nature, by the addition of a sufficient quantity of a strong acid or one of its salts. The material first appears in the form of flakes, which deposit at the bottom of the liquid or come to the surface, depending upon the density, or whether bubbles of gas are formed during their precipitation. Two phenomena are then distinguished successively and perhaps independently of each other, that of *flocculation* and that of *sedimentation.**

The proportion of salt or acid necessary to flocculate the pseudo-solutions must exceed a certain limit, very small, it is true, in order to be efficacious; for example, with a turbidity formed of pure kaolin, the limit of action seems reached when the dilution of the acid is $\frac{1}{1500000}$ (C. Bodländer). In a general way, it is the salts of the polyvalent metals which are more active, and this fact holds good so much the more in proportion as the metallic oxide is weaker as a base, as is shown in the following table of the clarifying powers of some salts, compiled by H. Schulze, assuming the power of potassium iodide equal to 1:

* W. Spring, *loc. cit.*

Salt	Clarifying Power
KI	1.
KCl	2.5
$CaCl_2$	80.
$MgCl_2$	182.
Na_2SO_4	2.3
$ZnSO_4$	60.
$Al_2(SO_4)_3$	957.
Al_2Cl_6	1518.

Bodies which yield poorly conducting solutions, on the contrary, generally retard flocculation; alcohol, however, accelerates the precipitation of certain colloidal salts, such as potassium fluosilicate.

When an electric current is passed through a turbid mixture or a colloidal solution, we notice that a clarification takes place at one of the two electrodes, according to the chemical nature of the suspended substances, while a flocculation is produced at the opposite electrode. W. Spring has even shown that the electric current frees the water from every particle in suspension to the degree of rendering the liquid *optically empty,* that is to say, representing no luminescence upon the passage of a powerful ray of light. This flocculating property of the electric current joined to the absence of flocculation by bodies which are poor conductors of electricity, has caused several writers to attribute the flocculating power of saline substances, which are electrolytes, to the presence of free electrical ions from the salts. The following observations of W. Spring* tend rather to cause this property to be attributed to the presence of bases and acids freed by the dissociative action of the water upon the salts in solution.†

This author has first proved that, in the clarification of colloidal solutions by the electric current, the transportation of the particles is accomplished in the direction anticipated, or in the opposite direction by the difference of electrical conductivity of the liquid and of the colloid; in the second place, that the clarifying power of electrolysis is not in proportion to their respective electrical conductivities. Then he has observed the method of flocculation of suspended

* *Loc. cit.*

† See the theory of electrolytic dissociation of salts in Chapter IV. and that of the dissociation by hydrolysis in Chapter III.

particles of mastic by different metallic salts, not by mixing directly the solutions, but by superposing the turbid layer upon the saline solution and allowing the liquids to diffuse freely. The flocculation soon begins and the flakes descend as far as the layer, where there is an equality of density between them and the liquid. With salts of different metals, it is observed that, at the end of equal periods of time, the degrees to which the flocculation has progressed are different, without the possibility of finding a simple relation with the coefficient of diffusion of the salts; it is merely observed that salts derived from polyvalent metals clarify the turbidity to a greater degree. Colored salts, like sulphate of copper, have permitted the exact determination of the cause of this difference; it has been shown with this salt that the flocculation is produced well above the region where the blue color is manifest, and some tests made with capillary pipettes at the top of the flocculated zone, have shown, in fact, the absence of copper, but on the other hand, demonstrated the presence of sulphuric acid. Likewise, with aluminium chloride, ferric chloride, magnesium chloride, zinc chloride, alum, W. Spring has always perceived in this part of the solution the presence of the free acid of the salt without the metal; on the other hand, the flaky deposits, collected from the above concentrated saline solutions and washed with water, have always revealed upon analysis the presence of the corresponding metallic oxides.

These experiments prove clearly that metallic salts are decomposed during their diffusion through the colloidal suspensions. The metallic hydroxide has inclosed the particles of the colloid and has precipitated them, while the acid has diffused into the colloidal solution, flocculating it on its own account; the colloidal matter acts then upon the metallic salt like the septum of a dialyser and becomes a sediment while associating itself with the metallic hydroxide. If the polyvalent inorganic salts are more active than those of the alkaline metals in producing flocculation, it is because their hydrolytic decomposition is much more marked; it is, besides, those salt solutions which become most strongly illuminated when they are traversed by a powerful beam of light,—consequently constituting themselves a colloidal solution of metallic hydroxide formed by hydrolysis—which have a very considerable coagulative power.

These experiments show also that the coagulation of colloidal solutions cannot be produced without an association of the suspended particles with the mineral substance; recent researches,

notably those of Whitney and Ober* seem even to prove that this association follows in a certain measure the mathematical laws of definite compounds. When the colloidal solution of arsenic sulphide is precipitated by chlorides of potassium, calcium or barium, the precipitate always contains metallic oxide of the salt, and the liquor contains on the other hand free hydrochloric acid. If the precipitate is subjected to prolonged washing, a part, only, of the metallic oxide is eliminated and the rest remains bound to the colloid in an irreversible manner. If the same colloidal solution of arsenic sulphide be precipitated by solutions of different chlorides, but of the same molecular concentration, one perceives that the weights of metals carried down, bound in an irreversible manner to the precipitated colloid, are proportional to the molecular weight of the metals; these weights are, in fact, for 200 cubic centimeters of a five per cent colloidal solution of As_2S_3, 0.020 gram of Ca, 0.076 gram Ba, 0.036 gram K. With solutions of the same salt of different concentrations, the amount removed by the colloid is in proportion to the concentration. Finally, if the precipitate is washed with the solution of another salt, the metal of the second salt replaces quantitatively the metal primarily bound in an irreversible manner to the colloid. Similar results, obtained by J. Duclaux† upon the precipitation of a colloidal solution of copper ferrocyanide by various salts, have led him to conclude that "the materials extracted by coagulation are only the simple substitution of the radicals of the precipitant for those which compose the colloid."

Rules for Washing Colloidal Precipitates.—Although our knowledge of the formation of colloidal precipitates is yet quite incomplete, the preceding results permit us, however, to determine the rules to be observed for their purification.

Whenever the quantity of mineral salts, bound in an irreversible manner to the colloidal precipitate, is insufficient by itself to produce the flocculation of the pure colloidal solution of the same body, washing upon the filter with pure water reproduces the colloidal solution of the precipitate, and the precipitate, converted again into a *pseudo-solution,* passes through the filter. It is necessary then to wash, not with pure water, but with a solution of an acid or a salt which can be easily eliminated by desiccation in a drying oven or by ignition. The decreasing order of flocculation being the following:

* Whitney and Ober, *Zeit. phys. Chem.,* xxxix, 630 (1902).

† J. Duclaux, *C. R.,* cxxxviii, 571 (1904).

salts of the polyvalent metals, and acids and salts of the alkaline earth metals. We are often unfortunately obliged to take the least efficient. One cannot, in fact, employ any other salts of polyvalent metals than those of mercury, which can be utilized only in quite limited cases, on account of the reactions which they can give on their own account. Acids can be employed only with precipitates with acid properties (as, for example, in washing titanic acid with acetic acid), or with salts particularly insoluble in even strong acids (washing AgCl with dilute HNO_3). For salts of the alkaline metals, we are limited to ammonium salts, easily volatilized by heat;—the chloride, nitrate or acetate.

We are then frequently obliged to introduce into the wash water, only bodies with a weak flocculating power; acetic acid or ammonium salts. The latter, having a smaller equivalent weight than the salts of potassium or sodium, have, moreover, the advantage of being more active than these latter for the same weights, according to the observations of Whitney and Ober.

Finally, we can deduce again from these observations, the following general rule, already sanctioned by use in a great many methods of analysis,—"Whenever an hydroxide is to be precipitated by an alkali in a solution containing salts of the heavy metals, it is necessary, when possible, to redissolve the precipitate in an acid solution and reprecipitate by ammonium hydroxide; one thus replaces the heavy metal removed by the precipitate in the first precipitation, by an ammonium salt, which is easily volatilized during the ignition of the precipitate."

In the second precipitation, the concentration of the heavy metals is in fact insignificant in comparison to that of the ammonium salts, and the *irreversible* impurity in the precipitate is almost exclusively formed by the latter. By repeating this treatment, one can finally obtain precipitates which, when ignited, are pure. This is a rule which must be followed, for example, in the precipitation of $Fe_2(OH)_6$ or MnO_2, in solutions containing an appreciable quantity of calcium salts, a very frequent occurrence in the analysis of minerals, oxides of iron, or manganese.

CHAPTER II

THEORETICAL PRINCIPLES OF THE ANALYTICAL METHODS BASED UPON IRREVERSIBLE REACTIONS

1. Principal Types of Irreversible Reactions Employed in Analysis

THE methods of separation based upon irreversible chemical reactions are extremely varied, by reason of the very different processes which this category of reactions offers in order to obtain systems of two distinct phases, separable by mechanical means. We will indicate by a few examples the principal types to which these methods belong.

Methods Based upon the Stability of Bodies at Arbitrarily Fixed Temperatures. — The transformation of a great number of precipitates into definite stable compounds at high temperature, at which many of the methods of analysis aim, belongs to this category. A great number of insoluble bodies obtained by double decomposition; metallic oxides, oxidized salts, etc., are, in fact, hydrates of a composition variable with the temperature and cannot serve directly in the exact determination of the elements which they contain. Others, like the sulphides precipitated from a salt solution by hydrogen sulphides, become more or less oxidized in air during their desiccation. By ignition, one can transform the hydrates of iron, aluminium, silica, etc., a great number of hydrated salts such as the oxalate of calcium, ammonium magnesium phosphate, etc., into oxides or anhydrous salts, generally crystallized and of a perfectly definite composition; thanks to the very great stability of these bodies at high temperatures. Likewise, by heating hydrated sulphides, more or less oxidized, in an atmosphere of sulphur or of hydrogen sulphide in a Rose crucible, one obtains the metallic sulphides, (MnS, Cu_2S, etc.), crystallized and of definite composition.

Finally, the unequal stability of different classes of salts, such

as the nitrates, the thiosulphates, etc., heated to definite temperatures, allows the formulation of numerous processes of separation.

Methods Based upon the Employment of Oxidizing and Reducing Reagents.—Most of the methods of attacking mineral substances by the *dry method* or the *wet method* belong to this category. They constitute an intermediate stage, a disintegration of a complex system which is transformed into a more simple system: decomposition of natural metallic sulphides by aqua regia or potassium nitrate, chromite by sodium dioxide, of wolfram by aqua regia, etc.

In certain cases, the reaction furnishes at the same time the determination of the substance: the oxidation at red heat, of alloys of lead and silver (cupellation), determination of the ash of combustible bodies by roasting in the air, etc.

The numerous oxidizing or reducing reactions used in volumetric methods (reduction of potassium permanganate by ferrous or manganous salts, the oxidation of sodium thiosulphate by iodine, etc.), or in the methods by precipitation (precipitation of MnO_2 by ammonium hydroxide and bromine or by hydrogen dioxide, of mercuric salts by phosphorous acid, of gold by ferrous sulphate or sulphurous acid, etc.), the ignition in air of bodies easily oxidized (ZnS, MnS, etc.) in order to transform them into oxides with a definite composition, belong equally to the same category.

Here may also be incorporated the eudiometric methods for the analysis of combustible gases, containing hydrogen or carbon, by combustion with an excess of oxygen. It is to be noted that these methods permit the analysis of a mixture of combustible gases only in the case of two gases whose nature is known: it is, in fact, in this case only that the data from the experiment (contraction of volume after combustion, volume of carbon dioxide produced) compared with the equation of combustion of the two gases, furnish as many equations as unknown quantities.

Formation of Soluble or Insoluble Complexes.—Another class of methods, very different from the preceding, consists in bringing a single one of the bodies of the system to be analyzed into a *complex* combination in which the common characteristics of the element are concealed from its ordinary reagents; the body in question can then be separated from the other bodies of the system on the basis of the solubility or insolubility of the complex formed, or again by a special chemical property of this complex.

Most metals can, in fact, form with ammonium hydroxide, alkali cyanides, organic bodies with alcoholic functions, etc., complex combinations in which their characteristic properties may be absolutely masked from their habitual reagents, because they are no longer exchangeable by double decomposition as in their salts, properly called, and are contained in these compounds under the form of a radical with several elements. The metalloids too have usually the same property, and the oldest known complexes are the oxygen acids of chlorine, which in these compounds have lost their fundamental property in chlorides, of making the double decomposition with the acid radical of silver nitrate. It is the entire complex, ClO_3 for example in the chlorates $MClO_3$, which will replace NO_3 in $AgNO_3$ by forming the soluble chlorate of silver instead of AgCl, insoluble in water.

The formation of these complexes is frequently a hindrance in analytical chemistry, because, at times, it renders the precipitation incomplete or prevents it altogether, but, inversely, this property may be utilized in bringing into solution insoluble bodies, or in keeping them in solution in spite of the presence of reagents which would reprecipitate them if they were not bound up in these special combinations. The principal complexes utilized in inorganic analysis are the following:

Ammonia redissolves easily quite a large number of metallic hydroxides (Mg, Zn, Ni, Co, Cu, Ag, etc.), by forming complexes with a basic function, which gives with the acid radical very soluble salts; the sesquioxides of iron and of aluminium do not form any, and this difference of property permits the very exact separation of the first metals from the latter. Among the ammonia complexes some are destroyed by prolonged boiling (chromium), others (copper, silver, nickel), are very stable even at this temperature. In general hydrogen sulphide and ammonium sulphide destroy easily these complexes when the sulphide of the metal is insoluble in water and in ammonium sulphide solutions.

The complexes formed by cyanogen and the alkali cyanides (ferro-, ferri-, cobalt-, cupro-cyanides) are of a still greater stability. It is for this reason that the alkali sulphides do not precipitate the copper of potassium copper cyanide or the iron of the ferro- and ferri-cyanides, that potassium hydroxide does not precipitate the cobalt from alkaline cobalt cyanides, etc. (reactions used for the separation of these metals from those which do not form any stable

complex cyanides; separation of copper and cadmium, of cobalt and nickel, etc.).

Most of the organic compounds which contain the alcoholic group OH, tartaric and citric acids (hydroxy acids), glycerine, sugar, etc., are capable of forming soluble complexes with the metallic hydroxides, the metal taking the place of the hydrogen in the organic compound, and the hydrogen of the organic hydroxyl giving water with the OH group of the hydroxide. The metal in this way loses all of its ordinary analytical reactions. Thus in inorganic analysis, one has to avoid especially the production of those complexes which may result, for example, from the transformation of the filter paper into soluble products by concentrated acids, for these organic complexes are so stable that it is necessary, in general, to evaporate to dryness and ignite the residue in order to destroy the organic matter. In certain cases, however, the formation of these organic complexes may be utilized in a particular determination. Thus by the addition of a great excess of citric acid to the acid solution of the natural calcium phosphates, which contain calcium together with iron and aluminium, the phosphoric acid alone can be precipitated by ammoniacal magnesium chloride, because all these other elements form with citric acid complexes not precipitated by ammonium phosphate in the presence of ammonium hydroxide, while ammonium magnesium phosphate is precipitated in spite of the presence of citric acid.

The acidimetric estimation of boric acid in presence of glycerine furnishes another interesting application of these organic complexes. Boric acid is too weak to be accurately titrated by an alkali in the presence of a colored indicator (see Chapter VII, § 1); if we add a large excess of glycerine a complex is produced (the radical BO replacing the H of the hydroxyl of glycerine) which is a much stronger acid than boric acid, and can be titrated accurately by the ordinary procedure.

Simple organic acids, such as acetic and oxalic acid,* not possessing alcoholic hydroxyl, do not give rise to the formation of such complexes.

In the cases we have just examined, ordinary insoluble precipitates are separated from other substances by means of soluble complexes formed by the latter. Inversely, the property possessed by

* A number of double oxalates are quite common and are used extensively in electrochemical methods.—*Editors' Note.*

certain metals or oxides, of forming with salts or other oxides *insoluble complexes,* may be utilized in their precipitation. Such is the case, for example, in the separation of thorium and cerium from the other rare earths, in the form of complex nitrates by the method of Wyrouboff and Verneuil* or of the analysis of special steels by the method of P. Nicolardot† employing the formation of ferric complexes containing the metalloids (P, As, Va, etc.) and not the metals. Prussian blue (Ferric ferrocyanide), would apparently serve for the separation and estimation of iron and, in fact, it was employed for this result in the eighteenth century; but it is too gelatinous to be completely freed from the impurities of the mother liquor.

2. Theoretical Principles Involved in Irreversible Reactions

Rôle of Speed of Reaction in Analysis.—Irreversible reactions, not being limited to a given temperature by the inverse reaction, present the advantage over reversible reactions of being *complete* in all cases, and of allowing the application of the reacting substances in the theoretical quantities. It is thus that these reactions give rise to the production of the definite compounds used in the calculation of the analysis; crystallized oxides, Fe_2O_3, Al_2O_3, Cr_2O_3, etc., obtained by the ignition at high temperature of hydroxides more or less constant in composition, of zinc oxide obtained by the roasting of the sulphides, etc.

But, in order that this use of the theoretical equation be legitimate, it is necessary that the reaction be accomplished in a complete manner in the interval of time in which one aims to realize it. Now the most complete reactions are far from being instantaneous, even when they appear to be very rapid; they are at times very slow when the system is maintained at a temperature a little below that at which the reaction is rapid, and we can even observe limits corresponding to *false equilibria.* It is thus that the detonating mixture of hydrogen and oxygen which, under the influence of the electric spark, combines suddenly and completely with explosion, gives place to a slow combination when heated below 560°, the temperature at which the combination takes place with explosion. At the boiling point of sulphur, one tenth only of the mass is combined at the end

* Wyrouboff and Verneuil, *C. R.,* cxxvi, 340 (1898); cxxviii, 1331 (1899).

† P. Nicolardot, *C. R.,* cxxxviii, 810 (1904).

of three days (Van't Hoff), and at 300° only 3.8 per cent of the mixture enters into combination, this limit being obtained at the end of thirteen seconds (A. Gautier and Hélier). The presence of inert gases, added to explosive mixtures, always decreases their rate of combination and plays the rôle of friction in mechanics, opposing the displacement of a body out of equilibrium; the water vapor produced at the beginning of the combination of hydrogen and oxygen at a low temperature in the preceding case probably produces the same effect.

In the ignition of mixtures of oxygen and methane, Mallard and Le Chatelier have observed a phenomenon of the same order, that of *retarded ignition;* the mixture of methane and oxygen ignites when heated above 650° but, at that temperature, a previous heating of ten seconds is necessary before ignition takes place, this retardation decreasing when the temperature rises and the interaction becoming instantaneous only at about 2300°. This phenomenon, without doubt, is not peculiar to this mixture, but it is clearly manifest only in this case.

These peculiarities are of very great importance in eudiometric analyses and methods related to them; they explain why it is often necessary to add detonating gas to combustible mixtures containing inert gases, in order that the electric spark give a complete reaction. For this reason, in the apparatus of the Orsat type, where the combustion of inflammable gases mixed with oxygen is produced by the incandescence of a platinum spiral, it is necessary to prolong greatly this incandescence in order to have complete combustion,—especially when the mixture contains methane. Finally, a too great excess of oxygen keeps the combustion of the inflammable gases from being complete in the calorimetric bomb, when one wishes to determine in it the calorific power of the combustible gas. The excess of oxygen plays the rôle of an inert gas, and it should be added in slight excess only of the quantity necessary for complete combustion.

Difficulties of the same order, arising from slowness of reaction or false equilibrium, may interfere in the ordinary dry or wet methods of analysis.

One must consider these, for example, in the production of the calcined oxides in the muffle furnace, or those obtained by the roasting of the sulphides. Here the criterion of complete reaction is easy, for it is sufficient to take from time to time the weight of the body and to ignite until two consecutive weighings, sufficiently

separated, give results exactly concordant, in order to be sure that the reaction is practically terminated.* Since experiments demonstrate that the speed of irreversible reactions, occurring with the evolution of heat, increases always with the temperature, it suffices, in general, to heat to a bright red heat for rather short periods of time, the length of which has been determined by experiment in each case (a few minutes to an hour at the most, in general). One is much less certain of arriving in a short time to complete reactions in operations by the wet method, where the temperature is often that of the laboratory and cannot exceed in any case the boiling point of the liquids employed, and where one has not at his disposal an indicator as sure as the invariability of weights.

The speed of reaction at a given temperature, we have been able to study quite easily for bodies in solution, forming homogeneous systems, and causing, while still homogeneous, a complete irreversible reaction.

From the observations of Berthelot† upon the decomposition of barium formate, verified and reduced to greater exactness by a very great number of later experiments, notably by those of Lemoine‡ on the action of oxalic acid upon ferric chloride, $Fe_2Cl_6+H_2C_2O_4=2FeCl_2+2HCl+2CO_2$, the speed of the reaction decreases in proportion as the mixture is depleted of the reacting substances and, at each instant, it is proportional to the active mass of the components present in the mixture. If then, we call p the initial weight of the components, y, the weight destroyed at the end of the period of time, t, the speed of the reaction $\frac{dy}{dt}$ obeys the law

$$\frac{dy}{dt} = k(p - y), \tag{1}$$

k having a positive value which depends upon the nature of the

* There are produced at times in the dry methods of analysis, incomplete reactions analogous to the false equilibria previously cited; it is thus, therefore, that the ignition, even greatly prolonged, of alumina and of stannic acid, containing a little sulphuric acid, does not expel all of the acid, in spite of the low stability of the sulphates. We obtain pure oxides only by heating a long time at a white heat, or by creating in the crucible, where the ignition is taking place, an atmosphere of ammonia, which combines with the acid, and the ammonium sulphate formed is volatilized.

† M. Berthelot, *Ann. Chim. Phys.*, (4) xviii, 147 (1869).

‡ G. Lemoine, *Ibid.*, (6) xxx, 289 (1893).

reaction and the temperature; we have then on integrating equation (1) in the case of an isothermic transformation where k is constant

$$\log\left(1-\frac{y}{p}\right)=-kt. \tag{2}$$

If we represent the time as abscissa and the quantities transformed, y, as ordinates, we see that this equation represents a curve starting from the origin and becoming tangent to a straight line, having $kp = \tan x$ for angular coefficient.

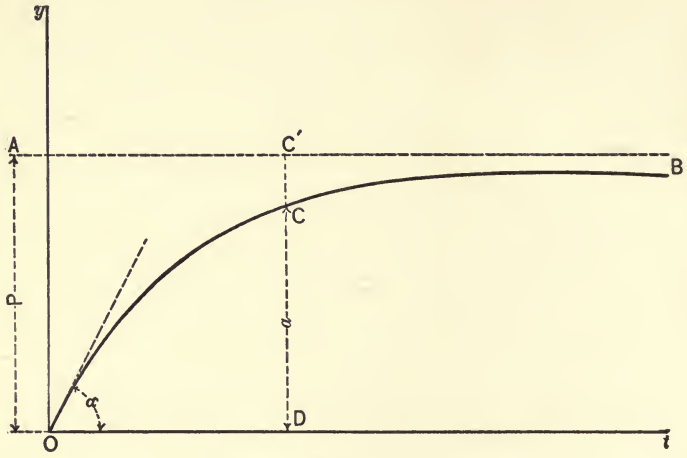

FIG. I

The second derivative $\frac{d^2y}{dt^2}=-k$, being always negative, the concavity of the curve is turned toward the t axis, and for $y=p=$OA the tangent is horizontal; the curve has then the straight line AB for asymptote and its course is that represented by Fig. I. The error which is committed in practice of assuming that the reaction terminates at the end of time $t=$OD, is the difference between C'D $= p$ and CD $= a$, or CC' $= p - a$; it is evidently smaller in proportion as the tangent at the origin becomes more erect (k is very large). In general, the elevation of temperature accelerates irreversible reactions, that is to say, increases the coefficient k which appears to vary with it according to an exponential formula $k = mA^{\theta}$, where m and A are coefficients dependent upon the reac-

tion and θ the temperature.* There is an advantage in operating at as high a temperature as possible. Hence the reaction between oxalic and ferric chloride which is practically complete in a few minutes at 100° in dilute solution, requires several years at ordinary temperature in order to be completed.

These considerations apply to most of the irreversible reactions by the wet method where the initial system is a homogeneous solution, even in cases where precipitates are produced. It is also necessary in these methods to pay close attention to the speed of reaction in order to avoid serious errors. In certain cases, for example, in action of iodine upon sodium thiosulphate, the speed of reaction is so great that we may regard the reaction as instantaneous. In other cases, however, for example in the precipitation of MnO_2 by bromine and ammonium hydroxide, the speed of transformation is quite slow, and the filtrate should always be tested for manganese, even after having allowed the reagents to react for some hours upon the warm solution.

Reactions Intermediate between the Initial and Final States. — It frequently happens that between the initial state of a chemical system and the more stable final state, in which it is to end more or less quickly, according to the conditions of temperature, concentration, etc., under consideration, there are intermediate successive reactions giving rise to bodies less stable than the final products, and which exist only a certain time and end by being resolved into the definite system. This observation is applicable especially to irreversible reactions, but it also takes place at times in reversible reactions.

Numerous examples can be cited in the domain of irreversible reactions. The solution of sodium thiosulphate treated with hydrochloric acid, gives as a final result the reaction:

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S:$$

but there is always formed an intermediary yellow solution of sulphur, the more stable the greater the dilution, and which later results in the above system with the sudden precipitation of sulphur.

The final reaction of hydrogen peroxide with chromic oxide in acid solution may be represented by the equation:

* G. Lemoine, *loc. cit.*

$$2CrO_3+2H_2O_2 = Cr_2O_3+2H_2O+5O,$$

but there is always produced, in the cold, a blue body, perchromic acid, subsisting during several seconds and so unstable that its exact composition is still unknown.

The formation of hydrogen peroxide itself is a stage of the same kind; the system $2HCl+BaO_2$ gives as the most stable term of the reaction $BaCl_2+O+H_2O$, but there is always formation of the less stable intermediate system $BaCl_2+H_2O_2$ which in the cold is still sufficiently stable for the utilization of this reaction in the preparation of hydrogen peroxide.

The reactions called "catalytic" involve equally the ephemeral formation of but slightly stable compounds serving as intermediaries between the initial system and the final state: formation of hydride of platinum in the combustion of the mixture of hydrogen and of oxygen at ordinary temperature (Berthelot), of hydride, carbonyl or ammonia in the numerous catalyses produced by nickel (Sabatier), etc. . . .

Organic chemistry offers innumerable examples of these successive reactions; the oxidation of alcohol by chromic acid or air in the presence of platinum black, which always gives aldehyde before acetic acid, the formation of all the explosive nitrated compounds, which constitute an unstable stage between the initial system and the final stable system of the products of explosive decomposition.

In the domain of reversible reactions, similar systems are more rare, but nevertheless, a certain number may be cited; formation of liquids supersaturated at the beginning of precipitation, the unstable double chloride and sulphide in the action of hydrogen sulphide on the chlorides of lead and of mercury, etc.

W. Ostwald, relying upon a great number of facts of this kind, has formulated the following principle under the name of the *Law of Successive Reactions.** "If we start with a system, representing the most unstable initial state, and if afterwards, we allow spontaneous transformation to take place, there is produced first, not the most stable final state, but on the contrary, the most unstable one which can exist after the initial state."

As a result of this one of the necessary conditions of quantitative

* W. Ostwald, *Die wissenschaftlichen Grundlagen der analytischen Chemie.* (3d English ed. p. 105.—*Editors' Note*).

analysis by chemical reactions, principally in the irreversible transformations, is to operate without haste, and to leave to the phenomena the time necessary to bring about the reaction in complete manner, experiment alone being able to furnish in each case the time necessary for the complete transformation of the system.

We shall see a little farther along, in the volumetric methods, some interesting application of the rôle which is played by the speed of reaction and the principle of successive reactions.

Thermodynamic Law of Irreversible Reactions. — In what concerns the realization of complete irreversible reactions, the law governing them is deduced from the principle of Carnot-Clausius and is expressed by the following equation applicable to every irreversible isothermic transformation:

$$(1) \qquad Q = T(S_A - S_B) + TP,$$

in which T represents the constant absolute temperature at which the reaction under consideration is carried out in the calorimeter; Q the quantity of heat liberated by the reaction; S_A and S_B the values taken in the initial state A and in the final state B, by the function S or *entropy,* defined by the equation

$$(2) \qquad S = \int \frac{dQ}{T},$$

dQ being the infinitely small quantity of heat which the system absorbs or evolves in the experiment along the cycle of transformation which it traverses and T, the absolute temperature at each point of the cycle. The expression $S_A - S_B$ is called according to Clausius, *compensated transformation* and the term $T(S_A - S_B)$ *compensated heat* (Duhem), whose value depends only upon the initial and final states of the system. The term P, called *non-compensated transformation,* has a value always positive, dependent, in general, upon the intermediate states between A and B of the system.* The expression TP or *non-compensated heat* represents the part of the heat Q set free by the reaction which is utilizable under the form of work (Le Chatelier).

* See *Introduction à la Mécanique chimique,* by P. Duhem (1893) Chap. ix and x, and *Lois générales de la chimie,* by G. Chesneau (1899) Chap. vi.

In order that a reaction may take place, the transformation must give a positive value for TP and, of all the transformations possible, the one which gives the maximum for TP corresponds to the most stable final state, since, once brought to this state, the system could no longer undergo any transformation except by giving a negative value to the term TP. From this is deduced the law which was established experimentally by Berthelot under the name of the *principle of maximum work:* this law may be expressed thus,*—*"If several reactions are possible the one which will finally tend to be produced will correspond to the production of maximum work."*

As the term $T(S_A - S_B)$ may be positive or negative, the value of Q may be negative, although TP is always positive. In practice, however, in all rapid reactions, the term $T(S_A - S_B)$ represents only a very small fraction (some hundredths) of the value of TP, which, therefore, gives a positive sign to the value of Q. In fact, in all irreversible transformations, chlorinations, oxidations, reductions, etc., employed commonly in inorganic analysis, the reaction *sets free* an important quantity of heat. Among the reactions which we have cited at the beginning of this chapter, those which set free the least quantity of heat are certainly the transformations of the amorphous hydroxides of iron, aluminium, chromium, etc., into crystallized anhydrous oxides which correspond to a simple allotropic change of desiccated oxide; the heat liberated has been measured for the sesquioxide of iron and found to be equal to +2.1 calories. It is quite sufficient to produce sudden incandescence of the amorphous oxide at the moment of its transformation into crystallized oxide.

3. Study of a Few Methods Based on Irreversible Reactions

From the preceding considerations it follows that, if an irreversible reaction, utilizable in inorganic analysis, is possible by virtue of the principle of maximum work, the only points to be examined in the discussion of methods based upon this reaction are the *stability* of the body employed in the determination, the *speed of reaction* and, if such are possible, the *intermediate reactions.* The study of the methods of analysis of this category requires consequently a profound knowledge of the individual properties of each compound employed in the method, and we can only say in a gen-

* Le Chatelier, *Sur le principe du travail maximum, C. R.,* cxv, 167 (1892).

eral way that at a given temperature, the stability of the body and the speed of the reaction are greater in proportion as the body under consideration is formed with greater evolution of heat.

We will content ourselves with giving here as examples of these discussions of methods; first: from the point of view of stability, two processes of separation based upon the unequal resistance of the same class of salts to decomposition by heat; the method *"of the nitrates"* of H. Sainte-Claire Deville, and the separations based upon the unequal stability of the thiosulphates in aqueous solution: second: from the point of view of the rôle which is played by the speed of irreversible and intermediate reactions, the volumetric methods by oxidation.

Method of Nitrates of H. Sainte-Claire Deville. — This method forms a part of a collection of analytical processes presented by their author with an exactness and a critical discussion entirely new in inorganic analysis at the time of the publication of the memoir containing them.* All properties of the bodies entering into the reactions are minutely studied, and the conditions for operating with maximum precision are exactly determined in it. This memoir then is of capital importance in the history of analytical chemistry, and it might still serve chemists publishing new methods as a model of precision in coördinating facts and deducing results. It would not appear useless then to recall here the principles which guided the author.

Deville designated this method as "the process of the *medium method,"* because the reactions utilized in it are intermediate between those of the wet method and the dry method. It permits the separation, with an accuracy which has not been surpassed, of the oxides of the alkalies and alkaline earths and of magnesium from the oxides Fe_2O_3, Al_2O_3 and MnO_2, bodies which are almost always associated in the calcareous rocks, the ores of iron and in numerous other minerals. The precipitation by ammonium hydroxide, which is employed habitually for this separation, has the disadvantage of carrying calcium and magnesium along with the colloidal hydroxides of iron, aluminium and of manganese, and it is in order to avoid this drawback, so clearly shown by him to exist, that Deville proposed his method of the nitrates.

This method is based on the unequal resistance of these nitrates to decomposition by heat and upon the different action of nitric

*H. Sainte-Claire Deville, *Ann. Chim. Phys.*, (3) xxxviii, 5 (1853).

acid as well as of ammonium nitrate upon the products of this decomposition.

From the point of view of their resistance to decomposition by heat, Deville arranges the metallic nitrates into four classes:*

1. *"Nitrates which liberate their acid in the state of nitric acid at a temperature little higher than that of boiling water, namely, nitrates of aluminium and ferric iron."*—The nitrate of aluminium readily melts in its water of crystallization, after which, at 140°, it sets free all of its acid and is entirely decomposed without the liberation of nitrous vapors in appreciable quantity. There remains an amorphous hydroxide of aluminium, very porous, analogous to pumice stone and very easy to wash. Ferric nitrate, still less stable, cannot even be evaporated to dryness without decomposition; nitric acid is evolved and pure oxide is left as a residue.

The oxides of iron and aluminium, thus obtained, are without action upon a hot concentrated solution of ammonium nitrate; they are, however, still soluble in dilute nitric acid.

2. *"Nitrates which liberate their acid at a slightly elevated temperature with production of nitrous fumes and formation of a superoxide; these are the nitrates of manganese, cobalt and nickel."*—If a concentrated solution of manganese nitrate is subjected to the action of increasing heat, brown flakes begin to separate from the liquid at as low a temperature as 140°. At 155° a rapid decomposition takes place throughout the whole mass, with the evolution of nitrous fumes, and the whole is transformed into pure anhydrous peroxide which forms a glittering layer upon the walls of the vessel. The peroxide thus prepared is insoluble in dilute nitric acid; hot concentrated nitric acid dissolves only traces of it.

The nitrates of cobalt and of nickel decompose almost like that of manganese, but at a rather higher temperature, giving black sesquioxides, which readily dissolve in dilute nitric acid with the evolution of oxygen.

Ammonium nitrate is without action upon the black peroxides of manganese, nickel and cobalt.

3. *"Nitrates which decompose with evolution of fumes and partial formation of basic nitrates at temperatures between 250° and 350°."*—The nitrates of magnesium and of zinc belong to this

* It is easy to verify that the order of stability given by H. Sainte-Claire Deville is indeed the same as that which is given by the heat of formation of the different nitrates under consideration.

class. A concentrated solution of magnesium nitrate boils at 170°; the distillate is pure water. From 210° to 310° a little pure nitric acid is set free, while it is only at about 330° that the first bubbles of nitric oxide are given off. At this moment, about one tenth of the acid of the nitrate has been set free and a basic nitrate has been formed which, on washing with water, leaves an insoluble residue of magnesium hydroxide with perhaps a little basic nitrate. Magnesium nitrate which has been heated to this point is, of course, soluble in dilute nitric acid, and is equally so in a slightly heated concentrated solution of ammonium nitrate, with evolution of ammonia. Zinc nitrate behaves in the same manner.

4. *"Nitrates undecomposable at the maximum temperature of the oil bath; this class includes the nitrates of the alkali and alkaline earth metals which decompose only at red heat and above."* The procedure proposed by H. Sainte-Claire Deville for the separation of these different oxides depends directly upon these different properties. We will summarize in a few words. All of the oxides are brought to the state of nitrates in solution by a suitable previous treatment; the solution is gradually evaporated to a temperature of from 200° to 250° or even a little higher until the disappearance of the nitrous fumes, if any are produced. From what we have just said, the residue is composed of:

Manganese dioxide Aluminium hydroxide Ferric hydroxide	Nitrate and basic nitrate of Magnesium	Alkali and Alkaline earth nitrates

The mass is moistened with concentrated ammonium nitrate, and heated, the operation being repeated at will, until there is no further evolution of ammonia, the quantity of which is ordinarily in direct proportion to that of the basic nitrates of magnesium (and of zinc) which have formed. It is allowed to digest at a mild heat after addition of water; the hydroxides of aluminium and iron and the dioxide of manganese remain alone insoluble, a mass quite dense and porous and very suitable for washing by decantation.* Diges-

* Deville indicates that, by reason of the presence of organic substances, or if the nitrates have been too strongly ignited, a little MnO_2 passes to the state of the lower oxide upon which the nitrate of ammonium reacts slightly. Some traces of manganese may thus pass into solution which are found later with the magnesium, from which it is easily separated; "but," he adds, with reason, "no method obviates this difficulty better than that of the nitrates."

tion of the residue in warm nitric acid of medium concentration dissolves the hydroxides of iron and of aluminium and leaves the dioxide of manganese as a residue.

Methods based on the Difference in Stability of the Thiosulphates.—Quite a large number of processes of separation are based upon the addition of sodium thiosulphate to cold or boiling neutral or slightly acid solutions of chlorides or sulphates of the metals. Sodium thiosulphate, a salt formed from a strong base and an acid of medium strength, produces double decomposition with the chlorides or metallic sulphates, for the reasons that will be explained in Chapter III, by reducing them, when such is the case, to the state of minimum oxidation. The equilibria toward which the reactions tend in this double decomposition, are constantly destroyed by many of the unstable thiosulphates decomposing spontaneously into insoluble sulphides and sulphurous acid (which itself reacts upon the thiosulphate in excess and gives sulphur, sulphur dioxide and sodium sulphate), so that finally one of the metals may be precipitated as the sulphide mixed with sulphur, while the metals forming more stable thiosulphates remain in solution.

The accuracy of the separations depends essentially upon the greater or less degree of stability of the different thiosulphates in cold or warm solution. They can be divided upon this basis into three groups.

1. *Thiosulphates decomposing more or less quickly when rapidly warmed.*—The thiosulphates of the metals of the copper family (except cadmium) and of tin, belong to this group. The addition of sodium thiosulphate to the soluble salts of these metals gives insoluble precipitates of the thiosulphates, which change into sulphids and free sulphuric acid. All of these reactions, which are exothermic, are accelerated by an elevation of the temperature. In solutions of the salts of silver, for example, a white precipitate is produced which becomes black very quickly; conforming to the following reaction:

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$$

In the case of copper salts, the blue liquid becomes brown by reason of the reduction of the cupric salt to the cuprous state, when there forms a yellowish white precipitate of cuprous thiosulphate which rapidly decomposes into the black sulphide Cu_2S, and sulphuric acid.

With warm stannous chloride, there is a precipitation of a complex mixture of sulphur, sulphide and oxychloride, while in the case of antimony only the sulphide Sb_2S_3 forms, the precipitation being prevented by the presence of free oxalic acid (A. Carnot) in the case of tin, but not for antimony. However, the red sulphide of antimony precipitated is slightly soluble in warm concentrated oxalic acid, as I have shown, and also in very dilute hydrochloric acid (2 per cent). The precipitation of antimony by sodium thiosulphate in boiling solutions, is complete only if the free acid of the solution is exactly neutralized by sodium thiosulphate.

Aluminium and titanium belong to this group.

In the case of salts of aluminium, a partial precipitate of sulphur and of the hydroxide of aluminium, is produced in the cold, the sulphide of aluminium being decomposed by water. The precipitation is not complete on account of the formation of the sulphite of aluminium, which, in the cold, is very soluble and quite stable; but, if we boil until all the sulphurous acid odor disappears, the aluminium sulphite, which is strongly hydrolyzed by heat, is entirely decomposed and the precipitation is complete (Chancel). The reaction may be represented definitely by the equation:

$$Al_2(SO_4)_3+3Na_2S_2O_3+Aq = Al_2O_3 \text{ hydrated}+3SO_2+3Na_2SO_4.$$

Titanium acts like aluminium.

2. *Thiosulphates, Stable when Cold, Rapidly Decomposed when Hot.* — Cadmium appears to be the only element that belongs to this class. If, to a cold solution of cadmium chloride sodium thiosulphate be added, a little cadmium is precipitated. The solution should be strongly acid, if all precipitation is to be prevented. By neutralizing the free acid, by an excess of sodium thiosulphate, and boiling, on the contrary, the thiosulphate of cadmium decomposes rapidly and there is a complete precipitation of cadmium in the form of cadmium sulphide CdS, as in the case of the metals of the copper family; by boiling in the presence of free oxalic acid, the precipitation of CdS is equally complete.

3. *Thiosulphates, Stable in both Hot and Cold Solutions.* — The thiosulphates of the magnesium series: Mg, Zn, Mn, Fe, Cu, and Ni, are soluble and stable in cold and warm solutions. If the solution is acid, the sodium thiosulphate is decomposed, forming an equally stable sulphite with the precipitation of sulphur. To cold

solutions of ferric salts, if sodium thiosulphate be added, a dark reddish brown solution is first formed, then sulphur is precipitated and a solution of ferrous sulphite is formed. It is only at a temperature above 100° that these thiosulphates, heated in a closed vessel, are decomposed with the formation of sulphides; at 130° for ferrous salts, at 120° for zinc salts; those of manganese do not precipitate (Gibbs). Salts of nickel and cobalt form the transition from the preceding class. I have verified the fact that at the end of twenty-four hours, sodium thiosulphate gives no precipitate in cold neutral solutions; on boiling, the liquor gradually becomes black, and deposits a little sulphide, but the precipitate does not form if the solution contains even a very small trace of free strong acid. It was observed, moreover, that, if we concentrate a solution of sodium thiosulphate at boiling temperature, by the addition of iron, nickel or zinc salts, the boiling point rises enough so that there occurs at a particular temperature, a precipitation of sulphur. This result is seen especially clearly in the case of nickel and zinc. It follows from this that, if in flasks that are partially filled with the solution and the walls of which above the liquid are not wetted, the solutions are heated considerably above 100°, the formation of sulphur upon the wall of the flask can be readily shown.

Finally, one may consider that the hot or cold thiosulphates of the manganese series are stable in acid solution and at temperatures not to exceed 100°. This is the same *a fortiori* with the thiosulphates of the alkali and alkaline earth metals, which, in any case produce by the action of acids only a precipitate of sulphur with the formation of the sulphite.

From this classification, it follows that among the numerous methods proposed for the separation of metals by the addition of sodium thiosulphate, only three are very exact, even in varying the initial acidity of the solution over quite a large range: (1) the separation of copper from all the metals of the manganese series (Method of Flajolot) in boiling solution slightly acidified with sulphuric acid, by the addition of sodium thiosulphate until there is no further precipitation of the black Cu_2S. The solution must remain acid and dilute and the dry walls of the vessel are not to be heated above 100°. (2) In the separation of iron and aluminium by the Chancel method, care must be taken to add sodium thiosulphate to the cold solution which has been slightly acidified with hydrochloric acid, to heat only after complete decoloration and to

keep at the boiling temperatures until the disappearance of all odor of sulphur dioxide. (3) The separation of cadmium and zinc in boiling solution slightly acid with oxalic acid, according to the method of Carnot.* The separation of tin and antimony in boiling oxalic acid solution, according to the method of Carnot† is capable of giving exact results, but on the express condition of neutralizing the free acid by the thiosulphate itself.

Finally, the separation of copper and cadmium by the action of the thiosulphate upon a cold acidified solution (Vortmann method‡), can only give very uncertain results, from what we have said above of the properties of cadmium thiosulphate.

Volumetric Methods by Oxidation or Reduction. — The principle of the volumetric methods is to form with the body to be determined in a solution a very definite reaction by means of a reagent of known strength, whose volume necessary for the reaction permits, from the equation representing the same, the easy deduction of the weight of the substance desired.

The condition which such methods must necessarily fulfil is that the exact moment at which the slightest excess of the solution used in titrating is added, beyond what is strictly necessary to produce the complete reaction, be indicated with great clearness by a very well defined phenomenon. In volumetric methods by irreversible reactions which are always phenomena of oxidation or reduction, we employ as oxidizing reagents, potassium permanganate or solutions of iodine in presence of starch, whose color is very marked; and the phenomenon marking the end of the reaction is the appearance or disappearance of this color, depending upon whether the reactions are of oxidation or reduction.

The distinctness of the phenomenon is evidently in proportion to the speed of the reaction. If we refer to the curve representing the speed of irreversible reactions in a homogeneous liquid (p. 34), and if we suppose the reagent added at the very first in a quantity exactly equivalent to that of the body to be determined, the curve shows that the color of the reagent will not disappear suddenly, but will change progressively, more quickly in proportion as the tangent to the curve is more erect.

For an extremely rapid reaction, like that of iodine upon sodium

* A. Carnot, *Ann. des Mines,* Aug. 1898.
† A. Carnot, *C. R.,* ciii, 258, July 1886.
‡ Vortmann, *Zeit. anal. Chem.,* xx, 386 (1881).

thiosulphate, the curve will meet its asymptote at the end of a very short period, a fraction of a second; for a much slower reaction, like that of potassium permanganate upon manganese chloride or even ferrous salts, it will occur only at the end of a much longer period, even at the boiling temperature, requiring several minutes.

If, as in the ordinary practical conditions, we introduce the reagent drop by drop, the first portions will be immediately decolorized because they correspond to that part of the curve where the tangent is nearly vertical; the last portions will give on the contrary, a slow decolorization, because they correspond to the points where the tangent approaches the horizontal.

Now, what is understood by the *appearance or the disappearance of a persistent tint,* is nothing definite, but depends upon the acuteness of vision of the operator, upon the arbitrary time between the introduction of drops of the reagent, and the estimate of the effect produced, etc. There is a moment when the speed of reaction will correspond, for example, to the point C of the curve (see page 45), that we will admit is the end of the reaction. The error introduced will be relatively measured by the proportion:

$$\frac{C'C}{C'D} = \frac{p-a}{p}$$

the variation in which depends upon the experimenter, and is larger in proportion as the reaction is slower.

All the volumetric methods based upon irreversible reactions are subject to the same source of error; however, one can overcome this almost completely by operating by *comparison,* that is, instead of estimating the substance to be determined according to the weight of the reagent contained in the corresponding volume of the titrated solution employed, the titration of the latter is determined by carrying out an identical operation with a solution containing a definite weight, p, of the substance to be determined, taken obviously with the same concentration as the first experiment. The relative error can then be greatly reduced; one can obtain, in fact, in this second experiment a curve similar to that of the first, and will obtain for the final point of the reaction a point corresponding to a value of the ordinate, a, by reason of a relative error, $\frac{p'-a'}{p'}$. The value to be taken for the substance to be estimated will be $\frac{a}{a'}$, while the exact

value is evidently $\frac{p}{p'}$, but, if we have experimented in the two cases in exactly the same manner, with the weights p and p' and concentrations as nearly alike as possible, we will have the same relative error in the experiments, that is to say, that we have

$$\frac{p'-a'}{p'} = \frac{p-a}{p}$$

from which we readily obtain $\frac{a}{a'} = \frac{p}{p'}$.

The result obtained is, therefore, rigorously exact if one has experimented under identical conditions, and it will be the more so in every case, as these conditions are approached.

It is due to this method of titration by comparison that we may count legitimately upon the exact results, even with methods giving quite a large relative error, providing that the latter be the same in all operations. This also explains the fact that two experimenters estimating in a quite different manner the end point of the reaction in a definite operation, can, however, obtain concordant results when they operate by comparison.

The same considerations are applicable to errors that may be made by reason of *intermediate reactions,* whose effect is added to that of the speed of reaction. A typical example in this respect is that of the estimation of manganese by the *Guyard-Volhard method.* The reaction utilized is the following:

$$(1)\quad 3MnCl_2+2KMnO_4+2H_2O = 2KCl+5MnO_2+4HCl.$$

As free hydrochloric acid would react in turn upon MnO_2 with the re-formation of $MnCl_2$, it is necessary to add a somewhat basic substance to react with the HCl without meanwhile precipitating manganous oxychloride upon which the oxygen of the air would act on its own account. With this object in view an excess of calcium carbonate, or more generally zinc oxide, is added.

The reaction of potassium permanganate upon manganese chloride while slow in the cold, is increased by heating and there is added to the hot solution standard $KMnO_4$ drop by drop; as long as any $MnCl_2$ remains, the permanganate produces immediately a brown coloration which rapidly changes into a precipitate and is deposited with the excess of ZnO. The reaction decreases little by little and finally one or two drops of the permanganate give to the supernatant

liquid a pink tint which persists for several minutes and the reaction is then considered terminated.

A solution of permanganate is standardized by comparison against iron according to the following known equation:

$$(2)\quad 10FeSO_4+2KMnO_4+4H_2SO_4 = 5Fe_2(SO_4)_3+2MnSO_4+4H_2O.$$

One cubic centimeter of the permanganate would correspond to n milligrams of iron and should according to equation (1) be equivalent to $n\times 0.2944$ milligrams of manganese. Now, the experiments of numerous technical laboratories indicate that it is necessary to substitute for the coefficient 0.2944 a notably different coefficient: 0.3104 according to Campredon,* 0.307 according to Wencélius,† and 0.304 according to Prost,‡ which correspond respectively to 94.8 per cent, 95.8 per cent, and 96.8 per cent of the quantity of permanganate required according to equation (1). Finally, other chemists, Ledebur|| and de Koninck§ hold that it is necessary to employ the theoretical quantity.

It is apparent from these values which are obtained from the very numerous comparative experiments performed with great care, that the difference between the theoretical quantity of permanganate and the quantity added in titration until the appearance of the persistent pink coloration varies from zero to five per cent, according to the experimenter. This difference depends, as shown by our own personal investigations, on the fact that, according to the method of the experiment, more or less oxide intermediate between Mn_3O_4 and MnO_2 is formed; such as, the manganite of manganese of Carnot, $5MnO_2{\cdot}MnO$ or Mn_6O_{11}, which, if it alone is formed, would correspond to the coefficient 75 per cent: or (such as) the (intermediate) oxide $9MnO_2{\cdot}MnO = Mn_{10}O_{19}$ of Meineke, which would correspond to the coefficient 84.3 per cent. Different authors, Gorgeu¶

* L. Campredon, *Guide pratique du Chimiste métallurgiste*, p. 472, Paris, 1898.

† A. Wencélius, *Méthodes d'analyse des laboratoires d'aciéries, Thomas*, p. 81, Paris, 1902.

‡ E. Prost. *Manuel d'analyse chimique appliquée.* p. 145, Paris, 1903.

|| Ledebur, *Leitfaden für Eisenh. Labor.*, 6th ed. p. 27, 1903.

§ L. L. de Koninck, *Bull. de la Soc. Chim. de Belgique*, January, 1904.

¶ Gorgeu, *Bull. Soc. Chim. de Paris.* (3) ix, 490 (1893).

and Carnot* have already called attention to the uncertainty of the results of the method of Guyard-Volhard due to the formation of this oxide; however, this method is in general use in the technical laboratories, where it is considered to give results as exact as the gravimetric methods.

In the following résumé of my verification of this method, I have carried out the experimental details described by the different authors and have, as a general rule, employed the usual conditions adopted in practice for the technical determination of manganese.†

With a very hot solution, by the addition of a large excess of pure precipitated zinc oxide (10 grams), the method of procedure of Campredon produces most quickly the settling of the precipitate. It was first shown that the solution is *completely freed* of $MnCl_2$ when about 85 per cent of the theoretical quantity of permanganate is introduced, which gives to the precipitate practically (deduction being made for the combination it can form with zinc oxide) the composition of the oxide of Meineke. From this moment, the reaction will take place between the precipitate already formed and the permanganate added. This reaction between two bodies, one a solid and the other a liquid, is very slow and its speed depends on the more or less colloidal physical state of the precipitate. Thus, as I have shown, the elevation of the temperature increases the speed, while the presence of basic bodies retards it and makes it finally incomplete even after boiling for several hours.

The unequal influence of these different factors allows the production, practically at will, of these *two* distinct *successive end-points* of the reaction for the same experiment. Starting with a boiling solution to which we add at once 10 grams of pulverized zinc oxide, then titrating immediately without reheating, shaking vigorously during 30 seconds after each addition of the permanganate, and allowing it to settle a moment to ascertain the tint of the supernatant liquid,—this operation lasting in all 15 to 20 min-

* A. Carnot, *Méthodes d'analyse des fers, fontes et aciers,* p. 101, 1895.

† That is to say, a quantity of pure $MnCl_2$, equivalent to exactly 0.200 gram of MnO_2, was dissolved in one-half liter of water containing one cubic centimeter of concentrated HCl. For the titration, I used six grams of pure permanganate per liter, and according to the equation (1), theoretically it would require 40.4 c.c. of this permanganate solution for the quantity of $MnCl_2$ solution used for the test.

utes,—the quantity of permanganate introduced, until the appearance of the pink tint, corresponds in a very constant manner to 95.8 per cent of the theoretical quantity (a value given by the coefficient 0.307 of Wencélius). If we then raise the liquid to the boiling point, it becomes decolorized, and if we continue the addition of permanganate until the reappearance of the permanent pink tint, by boiling one or two minutes between each addition, we obtain a second value, less constant than the first, corresponding on an average to 97.5 per cent of the quantity of permanganate; the pink tint then persists for more than twenty-four hours after cooling.

The two values of the reaction obtained, the first without reheating the liquid, the second by boiling it more or less after each addition of permanganate, become the same whatever may be the order of operation, but with varying coefficients. Here are examples of those that I have obtained:

	1ST VALUE	2D VALUE
HCl neutralized by $CaCO_3$ in great excess (10g)	94.6	98.0
HCl neutralized by ZnO in great excess (10g)	95.8	97.5
HCl neutralized by ZnO without excess	98.5	99.3
HCl neutralized by Sodium Acetate in large excess	97.3	100.2
HCl not neutralized (solution to acid $\frac{1}{600}$)	95.8	(A)

(A) With free HCl the second value cannot be exactly obtained, the acid by prolonged boiling decolorizing the permanganate far beyond the theoretical quantity. In this case the precipitate assumes a gray black color of pure MnO_2, while in all the other methods of operation, the color of the precipitate is more or less brown, denoting the presence of oxides lower than MnO_2.

If we maintain the liquid constantly at 100° during the whole test, the two values unite naturally into one (the second of the preceding table). In particular, by exactly saturating HCl with ZnO without excess, which is the method of de Koninck, a coefficient of 99.5 to 100.00 is obtained, which agrees with the theoretical value, as that author has rightfully indicated; likewise, the same holds with sodium acetate. In these two cases, the oxide of manganese formed is much more gelatinous than in the presence of ZnO and remains longer in suspension; one understands then how it can act much more completely upon the permanganate. But it should not be concluded from this that, in this case, the reaction is represented by the theoretical equation. Upon filtering the liquid after having added 86 per cent of the theoretical amount of permanganate, I have employed but 7.3 per cent to finish the titration

upon the precipitate. The precipitate is then still at this point a lower oxide than MnO_2.

Finally, to insure myself that oxides lower than MnO_2 when warm are very susceptible to reacting upon permanganate, I prepared the oxide of Carnot, Mn_6O_{11}, and verified the fact that at the boiling temperature it is capable of decolorizing up to 13.5 per cent of permanganate.

In substance, the value of the reaction depends then essentially upon the manner of operating, which leaves more or less saline oxide in the precipitate, depending upon the speed of the operation and the intermediate reactions which are produced. But in spite of the differences which the variety of coefficients proposed denote, the method of Guyard-Volhard is, however, capable of giving exact results, provided that the permanganate be standardized against a standard solution of manganese chloride,—and provided that the same procedure is followed in all of the operations. According to what we have said, the relative error, which is measured by the coefficient adopted, then always remains the same, and the estimation is still susceptible of a very acceptable precision.*

* The choice of method depends upon the kind of determination one has in view. Upon taking into account the rapidity of settling of the precipitate, greater with excess of ZnO than without excess, to operate with a large excess of ZnO (10g) added to the boiling and very slightly acid solution of $MnCl_2$ and titrating without reheating in 15 to 20 minutes, appears to me to be the best method suited to all cases from the richest pyrolusite to the steels, containing 0.4 per cent of manganese.

CHAPTER III

STUDY OF DOUBLE DECOMPOSITION BY THE CALORIMETRIC METHOD

Reversible Reactions in Analysis. — The most frequent case of operations to be accomplished in analysis is that of a homogeneous liquid containing, in an aqueous solution, the different elements to be determined, in the form of saline substances. We seek then by adding to the solution a suitable reagent, acid, base or salt, to form with one of the elements contained in solution, a *gaseous body* or an *insoluble precipitate* which is itself an acid, a base or a salt, produced by *double decomposition* among the elements of the solution and the reagent introduced. The separation of the elements under consideration ought to be practically *complete,* that is to say, that the gas or the precipitate which is eliminated ought to contain the totality of the element with a degree of approximation of the order of sensibility of the apparatus employed in measuring the same.

The point of view which should be adopted in analytical chemistry is the one which guided Berthollet in his investigations of the "Chemical Statics" of double decompositions and whose results may be summed up in the following statement,—*"The decomposition of a salt by an acid, a base or a salt is more complete in proportion as there results, from the exchange of the acid group and metal, a less soluble or more volatile compound than the reacting bodies under the conditions of the experiment.*

In fact, upon this empirical law have been founded almost all of the methods of analysis based upon the *chemical precipitation of definite compounds* whose weight permits one to calculate the weights of the elements thus separated in the insoluble state in the midst of a liquid easy to separate by filtering the precipitate or separating themselves by volatilization in the gaseous state. But there is no acid, base or salt strictly insoluble in water, and the precipitates considered in analytical chemistry as the most insoluble, ammonium magnesium phosphate, barium sulphate, etc., have in reality a solubility of the order of one millionth in pure water, that is, one liter of pure water contains from one to two milligrams when saturated. a weight which exceeds considerably the accuracy of our

apparatus. From this point of view, it is apparent that small volumes must be employed in analytical chemistry. Precipitation is, then, never absolutely complete, owing to the slight solubility of the precipitates in pure water, and the experiments show that this solubility is frequently increased by the presence of the reagents already introduced, or of the products of the double decomposition that gave the desired precipitate. It is thus that the solubility of silver chloride in water, which is practically zero when the water is pure or only acid with nitric acid, becomes very appreciable in the presence of the sodium nitrate which is necessarily produced in the precipitation of silver by the method of Gay-Lussac in which the precipitate of silver chloride is formed by double decomposition between silver nitrate and sodium chloride.

In a general way, double decompositions or reciprocal actions of acids, bases and salts, yield *incomplete reactions,* limited by the reverse reaction,—or *chemical equilibria,*—even when there is produced a precipitate insoluble in water or a volatile body; and the almost exclusive object of inorganic analysis ought to be the research for conditions in which the equilibria of these *reversible reactions* can be displaced in the direction of *practically complete reaction.*

The same study imposes itself more strongly upon the volumetric methods, so numerous to-day, utilizing the double decomposition, no longer to obtain a definite insoluble compound, but a reaction in the solution without precipitation, the end of the reaction being simply indicated by a change of color due to an excess of the reagent added.

The study of these conditions may be carried on by two different methods:

1. A method which I shall call *Calorimetric,* consisting in considering exclusively the reacting masses and the heat change in the double decompositions, and in utilizing the data of the calorimeter in order to interpret the direction of the displacement of the equilibrium by the aid of the principles of thermodynamics. This method will permit us to explain the processes of analysis based upon double decompositions without forming any hypotheses upon the constitution of the salt molecules in aqueous solutions. It admits the fact alone that heat is the only mode of energy capable of variation in the system in which the chemical reaction is produced, realized in the calorimeter at an obviously constant temperature. The energies corresponding to the electric state, luminous

state, etc., of the system, are then supposed to be constant or, at least, to occasion variations of a magnitude negligible in comparison to the calorific effects, which represent well the conditions realized in the practice of inorganic analysis.

2. A method which we can call *Electrolytic,* which attributes to salt solutions a hypothetical molecular constitution based upon the manner in which they act under the influence of an electric current produced by a source outside of the solution and dividing the dissolved molecules into two elements or groups of elements called *ions,* set free at the electrodes: H and Cl for HCl, 2K and SO_4 for K_2SO_4, Na and OH for NaOH, etc. In this method, we admit, (and this is what constitutes the hypothesis), that, in salt solutions *not subjected to an electric current,* and whose electric charge is consequently constant, the molecules are more or less dissociated into free ions which alone play the active rôle in double decompositions. We extend, moreover, to the masses of the ions and the undissociated molecules, the laws of equilibrium drawn from the principles of thermodynamics, but without specifically incorporating the heat effect of the reactions, which, in this method, is replaced by the *electrical conductivity,* corresponding to the degree of dissociation of the chemical molecules into free ions. The electrolytic method, which is that adopted by Ostwald in his *Scientific Foundations of Analytical Chemistry,* is certainly more attractive, *a priori,* than the calorimetric method, in that it is attached to the general theory of Arrhenius, permitting coördination of a large group of phenomena, abnormal in appearance, in the most varied domains; osmotic pressures, freezing points, boiling points, electrical conductivities, etc. But, as we will see later, numerous facts have been established in these later years, notably by Professor Kahlenberg of the University of Wisconsin, which cast a certain doubt upon the legitimacy of the extension of the electrolytic theory to the concentrated salt solutions which are commonly employed in inorganic analysis, and under these conditions, it appears to us preferable in order to explain the processes of analysis, to have recourse to the calorimetric method, which is surely free from hypotheses and appeals only to the reaction taking place. Moreover, the two methods will be successively described and, in the theories which I will present in the course of this work upon a few of the operations of inorganic analysis founded upon double decomposition, I will take care to indicate the electrolytic explanation of

Ostwald beside the calorimetric explanation, giving the reasons which seem to me to militate in favor of the latter.

The study of double decomposition made from the calorimetric point of view with which we shall begin, will be divided into three parts: in the first it will be shown how we can follow the processes of double decomposition by means of the calorimeter; in the second, we will present the successive developments which the notion of chemical equilibrium has taken in double decompositions, studied from a purely experimental point of view; finally, in the third, we will indicate the mathematical expression of the law controlling these equilibria established by means of the principles of thermodynamics, and we shall see in what measure it is in accord with the facts established by experiment.

1. Thermal Changes in Double Decompositions

The immense work of thermochemistry produced by Berthelot conveniently furnishes all the data necessary for the study of double decompositions, from the point of view of inorganic analysis.

Neutralization of Acids by Bases. — The point of departure in order to understand the reactions which are produced in the mutual reaction of two salts in solution, is the calorimetric study of the neutralization of acids by bases. On one hand the same acid dissolved in water sets free very different quantities of heat with different bases, and on the other hand the same base sets free very different quantities of heat with different acids. This is shown by the following table for the principal acids employed in inorganic analysis and for a few bases chosen as types in each family of metals. The table giving the heat of formation of salts at 15° obtained in a dissolved or precipitated state, by neutralization of the base and of the acid dissolved generally as one half equivalents per liter.

Bases	$\frac{1}{2}H_2SO_4$	HCl	HNO_3	$HC_2H_3O_2$	$\frac{1}{2}CO_2$	$\frac{1}{2}H_2S$
	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.
NaOH	15.85	13.70	13.70	13.30	10.20	3.85
$\frac{1}{2}Ca(OH)_2$	15.60	14.00	13.90	13.40	10.50	3.90
NH_3	14.50	12.45	12.60	12.00	5.35	3.10
$\frac{1}{2}Zn(OH)_2$	11.15	9.85	9.80	8.90	5.50 (solid)	9.60 (solid)
$\frac{1}{6}Fe_2(OH)_6$	5.70	5.90	5.90	4.50	.....	.....
$\frac{1}{2}Cu(OH)_2$	9.35	7.50	7.50	6.20	2.40 (solid)	15.80 (solid)
$\frac{1}{2}Ag_2O$	7.25	2.06 (solid)	5.20	4.70	6.90 (solid)	27.9 (solid)

From this table we can classify the acids into *strong, medium,* and *weak,* and likewise the bases into *strong, medium,* and *weak,* according to the quantities of heat liberated in the process of neutralization; 13.50 Calories at least for strong acids and bases, 13.50 to 12 for the medium, and below 12 for the weak. The determinations made by Berthelot have shown that the reciprocal displacement of acids or of bases in salts is more complete in proportion as the difference of the heat of neutralization of the same base by two acids is greater, and conversely. The displacement is practically complete if the difference is very large, partial if it is small, as is shown by the following two typical examples* of these reciprocal displacements:

Displacement of a medium base by a strong base:

$$NH_4Cl + NaOH = NH_3 + NaCl + H_2O + 1.07 \text{ Cal.}$$

The total displacement would correspond to 1.25 Cal.

$NH_3 + NaCl$ sets free only -0.05 Cal. which shows that the displacement of NaOH, a strong base by NH_3, a medium base, is extremely small.

Displacement of a medium acid by a strong acid:

$$NaC_2H_3O_2 + HNO_3 = HC_2H_3O_2 + NaNO_3 + 0.45 \text{ Cal.}$$

The thermal change is obviously equal to the difference of the heat of neutralization of sodium hydroxide by the nitric acid and by acetic acid; the reaction is almost complete. The inverse reaction of acetic acid upon sodium nitrate liberates only -0.06 Cal.; the action is very weak, but not null, however. It is known, in fact, that traces of hydrochloric or nitric acids can be easily liberated by boiling an alkaline chloride or nitrate with an excess of acetic acid.

Action of Water upon Salts in Solution; Phenomena of Hydrolysis. — If we measure the quantities of heat evolved in the neutralization of acids by bases in solution in volumes of water more or less large, we ascertain that the heat of neutralization diminishes in general when the dilution increases. It decreases very little when it is a question of strong acids acting upon strong bases, notably with weak acids and strong bases and reciprocally, finally, in a con-

* Berthelot, *Essai de mécanique fondée sur la thermochimie,* II. 689-593 (1879).

siderable proportion with weak acids and bases. This is shown by the following examples.*

	Volume		Differences of Calories Liberated
	4 Liters	24 Liters	
$KOH + HNO_3$	13.83	13.76	—0.07
$H_3BO_3 + NaOH$	11.74	10.91	—0.83
$H_3BO_3 + NH_3$	9.44	7.27	—2.17

Of course the values obtained from the calorimeter are corrected for the thermal effect produced by the increased quantity of water acting separately upon the acid and the base, a very marked effect when the base forms hydrates with evolution of heat.

The difference between the numbers in the first two columns of the preceding table, or heat absorbed on dilution, can be equally well obtained by beginning with the salt completely formed, dissolved in four liters and adding water, which gives the same results conforming to the principle of the initial and final states.

The thermal effect of the dilution is produced completely in a few seconds, as, moreover, is that of the neutralization of the bases by acids.

The heat absorbed by dilution can be explained only by an interaction less and less complete, of acid and base in proportion as they are diluted by a larger volume of water, or reciprocally, by the dissociation of the dissolved salt into free acid and free base, the greater in proportion as the salt is diluted. Following the principle of thermochemistry, the degree of dissociation when one passes from a given concentration to a weaker concentration, is equal to the ratio of the heat of dilution to the heat of formation of the salt in the initial concentration. It is this decomposition of the salt molecules by water into free acid and free base that is termed *hydrolysis.*

One could be tempted to attribute the thermal effect of the dilution to an action of water upon the dissolved body, other than the separation of the salt into its two components which have become partially free; but a great number of well-known reactions place the phenomena of hydrolysis beyond doubt and an uninterrupted chain of intermediate reactions can be easily established between the

* *Ibid.,* II. p. 216.

cases where hydrolysis is manifested by a tangible phenomenon and those where it is explained, as in the cases examined above, only by a thermal effect. The great importance of the phenomena, of the comprehension of the double decompositions, and the explanation of the methods of analysis which are derived from it, require us to enter upon the subject in considerable detail.

In a certain number of cases, the decomposing action of water upon salts is shown by the formation of an insoluble or volatile product, as in the action of water:

1. Upon chlorides of antimony and of bismuth, giving insoluble oxychlorides with a marked evolution of heat:

$$BiCl_3+H_2O = BiOCl+2HCl+7.8 \text{ Cal.}$$

2. Upon mercuric sulphate with the formation of a precipitate of the basic sulphate:

$$3HgSO_4+2H_2O = H_2SO_4+HgSO_4\cdot 2HgO.$$

3. Upon ferric chloride which gives, especially in warm dilute solution, a precipitate of ferric hydrate or oxychloride:

$$Fe_2Cl_6+6H_2O = Fe_2(OH)_6+6HCl.$$

The same is true in the case of ferric acetate, which is still more easily hydrolyzed and more completely than the ferric chloride, and with stannic salts, titanium salts, etc.

As examples of the production of volatile bodies; bicarbonate of sodium is decomposed in dilute solutions into the *neutral* normal carbonate and free carbon dioxide which remains dissolved but which one can readily show is present by passing through the solution an inert gas, hydrogen, for example, and bubbling this current of gas through lime water. In many cases it is sufficient to evaporate a solution and condense the vapors when a little acid of the salt is found. Thus, the distillation of a solution of zinc acetate gives acetic acid, that of ferric nitrate, nitric acid, etc. The hydrolysis of solutions of ammonium salts, even of strong acids, can be rendered manifest as Berthelot* has shown by distilling dilute solutions of these salts; ammonia, freed by hydrolysis, and very volatile, is released, while the acid, which forms with the water a much more

* *Ibid.*, II. 219.

stable combination, remains in the distilling flask and makes the liquid more and more acid. An alkaline test of the distillate and an acid test of the residue show the presence of free acid and free base, and enable the estimation of the proportion of salts decomposed. By employing 10 grams of salts dissolved in 250 c.c. and by collecting the distillate until about one half of the volume is distilled off, Berthelot found that the following decomposition was produced under these circumstances:

For the chloride 1 thousandth part
For the nitrate 2 thousandth part
For the sulphate 5 thousandth part.

This proportion is greater for salts of organic acids, which are much more strongly hydrolyzed than the preceding salts of strong acids.*

Finally, in certain cases, we can produce hydrolysis by the indirect reaction of the acid or the free base of the hydrolyzed salt; if, for example, to a concentrated solution of sodium borate, colored blue by litmus, acetic acid is added until the red tint just begins to appear, and if it is then diluted with a large quantity of water, the blue color will reappear, demonstrating the liberation of alkali. We can equally well prove the production of free sodium hydroxide in the dilute sodium borate by adding silver nitrate to a concentrated solution of this salt which precipitates white silver borate, then to a very dilute solution which precipitates brown oxide of silver (Rose).

The hydrolysis of ammonium chloride can be demonstrated by adding phenolphthalein to a concentrated solution of this salt and then enough ammonium hydroxide to make the solution distinctly pink; by then diluting the solution with water, the pink coloration disappears by reason of the liberation of a little hydrochloric acid (Ostwald).

In the saponification of esters by water, which is related to the phenomenon of hydrolysis, the liberation of acid is manifest likewise by the increasing acidity of the water up to a certain limit.

* This decomposition of ammonium salts by water at the boiling temperature ought always to be considered, in the precipitations made by the addition of ammonium hydroxide to boiling acid solutions of salts of iron (ferric), aluminium, etc. In many cases, in order to obtain a more complete precipitation there is a tendency to add a slight excess only of ammonium hydroxide and to heat a long time in order to expel this excess and collect the precipitate; but it is necessary to be very careful to verify at the end that the liquid has not become acid, in which case the precipitation is necessarily incomplete.

Dialysis can reveal the production of the acid liberated in hydrolysis of a great number of salts formed of strong acids and weak bases; the acids being *crystalloids* and the bases *colloids,* the first alone permeating the membrane of the dialyzer.

Finally, we can, in certain cases, bring into evidence the hydrolysis of salts of weak acids or bases, by the following process, based upon the phenomena of absorption (described in Chapter I, § 1). We have seen that filter paper has a greater absorbing power for bodies with basic properties than for those of an acidic nature. If, then, a few drops of a dilute solution of a strongly hydrolyzed salt be allowed to spread upon a sheet of filter paper, the hydrate will be fixed upon the paper by absorption at the center of the disc, formed by the spreading of the liquid; while the water, containing no longer anything but acid, will withdraw toward the periphery, and, with a proper reagent, one can determine the zone beyond which the hydroxide has not passed. I have thus ascertained that a concentrated solution (10 per cent) of lead acetate spreads out uniformly upon the filter paper. If we mark the limit obtained and place the paper in an atmosphere of hydrogen sulphide, the disc turns uniformly black; but, with a 0.5 per cent solution, the result is entirely different, the hydrogen sulphide blackens nothing more than the center of the disc upon which the hydroxide of lead is precipitated by absorption, and the water, which is absolutely free from lead acetate, has diffused several millimeters beyond the clearly defined zone.*

All the cases of hydrolysis enumerated above, which are placed beyond a doubt by incontestable chemical reactions, are accompanied by heat effects (positive or negative, according to the case) in a ratio with the proportion of the salt decomposed by water. It is seen that between an hydrolysis like that of bismuth chloride, belonging in the category of very active chemical reactions with a large evolution of heat, up to the hydrolysis of ammonium salts of

* This experiment, which is easy to repeat with very dilute solution of numerous salts of heavy metals, explains why washing alone is incapable of removing the oxide thus precipitated, which has formed a union with the paper; this, in many cases, necessitates washing with acidulated water, in order to eliminate completely from the filter and from the precipitate the oxide of the metal contained in the filtrate (washing of barium sulphate precipitated in the presence of ferric solution, according to the Arnold method for the determination of sulphur in iron, cast iron and steel, of lead sulphate precipitated in the presence of copper, etc.)

the strong acids, almost imperceptible in the calorimeter, all intermediate cases are encountered and are demonstrated by irrefutable phenomena.

In a general way, experiments show that hydrolysis increases with the dilution, whatever may be the sign of thermal change. It generally increases with the temperature, because these reactions almost always absorb heat which is the habitual case of simple dissociations into free acid and base. When heat is liberated (the cases of hydrolysis of the chlorides of antimony and of bismuth giving insoluble oxychlorides) the hydrolysis diminishes with the temperature conformably to Le Chatelier's *principle of the opposition of the reaction to further change,* which has been formulated in all its generality by its author, precisely apropos of the anomaly which the hydrolysis of antimony chloride appeared to present in comparison to other known hydrolyses like that of mercuric sulphate.*

The speed with which hydrolysis occurs is extremely variable. The limit is obtained almost instantaneously within the calorimeter, for all the decompositions in which the water is not itself decomposed and forms only soluble hydroxides with the two parts into which the molecule of salt is subdivided. This is the case of all the hydrolyses of inorganic salts that do not precipitate upon solution, as ammonium salts, sodium borate, etc., where the heat effect is produced in a few seconds, as in the neutralization of acids by bases. It is not the same in the case in which the molecule of water is to divide in order to give with its elements, new groupings with those of the hydrolyzed bodies, as in the hydrolysis of ferric chloride, the saponification of esters by water, etc.:

$$Fe_2Cl_6+6H_2O = Fe_2(OH)_6+6HCl$$
$$CH_3COOCH_3+H_2O = CH_3COOH+CH_3OH.$$

Reaction is then decreased in general by the preliminary work of decomposition of the intervening molecules of water and the limit is often long in being attained, notably in the hydrolysis of esters. However, in the analogous case of salts of bismuth and of antimony, the limit is reached in the cold in a few minutes, to such a degree that one can determine quantitatively the bismuth in the form of the oxychloride by precipitating with an excess of water. The same is true for ferric acetate, when precipitated hot in the

*H. Le Chatelier, *C. R.*, c, 737 (1885).

form of the basic salt. On the other hand, the decomposition of stannic and titanium oxysalts is accomplished by boiling for a very long time. We will see later some very important applications in analytical chemistry of these unequal speeds of hydrolysis.

Hydrolytic dissociations are, moreover, phenomena of equilibrium, in which the direct reaction is limited by the reverse reaction, and are easy to realize by putting the products of the direct reaction in contact in water. The verification of the reversible character as related to the concentration factor is very simple for salts which hydrolyze instantaneously, like the alkali borates. For example, the absorption of heat, when its volume of water is added to a solution of ammonium borate, containing one equivalent in four liters, is —1.0 Calorie and, if the ammonium borate is produced directly by the saturation of the acid and base, the following is obtained:

H_3BO_3(1 eq. = 2l)+NH_3(1 eq. = 2l) liberates 9.44 Calories
H_3BO_3(1 eq. = 4l)+NH_3(1 eq. = 4l) liberates 8.44 Calories
Difference 1.00 Calorie

The limit of combination is then rigorously the same as the limit of decomposition for the same dilution. With hydrolyses causing insoluble precipitates, the same verification is rarely possible, on account of the physical transformation of the precipitate (polymerization, without doubt), in the cases, and these are most frequent, where the precipitate is of amorphous (colloidal) nature, and becomes rapidly insoluble in free acid, having lost the function of a normal hydroxide. The studies of Le Chatelier, upon the decomposition of mercuric sulphate by water, in which the precipitate is of crystalline nature and does not undergo physical modifications, leave in all cases no doubt of the influence of the concentration upon the character of reversibility.

The same observations also show the dependence of these reversibilities upon the temperature. Salts of simple hydrolysis, giving only soluble products, return to the initial state after heating, as Berthelot has shown in a number of cases by the determination of the heat liberated by the addition of one equivalent of sodium hydroxide to one equivalent of the salt before heating and after cooling. The heat liberated is the same. But, if there is produced by hydrolysis, an amorphous precipitate which is modified by heating, or by standing for a considerable time, as in the case of ferric salts, necessarily the system no longer returns to the initial state

after long heating. For example, ferric acetate, which is very readily hydrolyzed when heated for some minutes at 100°, then cooled to the ordinary temperature, is entirely decomposed, for potassium hydroxide gives an evolution of +12.72 Calories and it is only at the end of a rather long time that the acetic acid has redissolved a very small part of the basic acetate precipitate. On the other hand, heating for a short time does not keep the sulphate and even the ferric chloride from returning to the initial state.* Measurements of the conductivity made by M. Foussereau, of solutions of ferric chloride at different temperatures lead to the same conclusions.†

Summing up, we can deduce from the numerous calorimetric measurements of salts in aqueous solutions that, in general, all salts are more or less hydrolyzed into free acids and bases (or, occasionally, into complex compounds such as salts called basic). Salts formed by a strong acid and a strong base are but very slightly decomposed (sulphates, nitrates, and chlorides of potassium and sodium for example). Salts formed by a strong acid and a weak base or reciprocally (ferric chloride, sodium borate), are notably decomposed by water. Finally, salts formed by a weak acid and a weak base (ferric acetate) are very extensively decomposed by water, and, at times, practically completely.

If we designate Q the heat of formation of a dissolved salt, starting from the acid and base dissolved in a little water, q the heat liberated for a definite dilution, then the ratio $\frac{q}{Q}$ will represent, as a general rule, the fraction of the salt hydrolyzed. As it is necessary to consider the heats of solution as well as the heats of dilution of the free acid and base, it is often quite difficult to determine the correction to give to the values determined by the calorimeter, in order to obtain the exact value of $\frac{q}{Q}$. As a result the calorimeter rarely gives the exact limit of hydrolysis and, in fact, it is by other methods applied only to hydrolysis of very slow speed that the study of these limits has been possible for a number of reactions otherwise restricted; but the general significance of the

* M. Berthelot, *loc. cit.*, II, 284 and following.

† Foussereau, *Ann. Chim. Phys.*, (6) xi, 383 (1887); (6) xii, 393, 553 (1887).

phenomenon is no less firmly established by them, and that suffices in order to understand the processes of double decomposition.

Mutual Action of Two Salts.—With this notion of hydrolysis of salts, we ought to consider the aqueous solutions of an inorganic salt as containing the non-hydrolyzed salt in equilibrium with the greater or less fraction of free acid and base. If, then, we introduce another acid into the solution, it will combine with the free base and the equilibrium will be destroyed; a new quantity of the salt in solution will be decomposed, and so on until a state of equilibrium is established. At this moment there will be in solution two salts, non-hydrolyzed and a certain portion of the two free acids and free base.

Likewise, if we mix the solutions of two salts differing in acid and base, there will be a mutual combination of the free acids and bases, causing a new decomposition of non-hydrolyzed salts, and finally, there will be established a new equilibrium among the four non-hydrolyzed salts in presence of a certain proportion of the two free acids and free bases, an extremely small proportion if it is a question of salts of strong acids and bases, and a notable decomposition, on the contrary, with salts of weak bases and acids. The reaction can be represented by the equation:

$$AB + A_1B_1 \leftrightarrow AB_1 + A_1B.$$

A and A_1 being the acid radicals, B and B_1 the basic radicals, and it being understood that the salts are partially hydrolyzed into free acids and bases.

As previously indicated, if we call Q the quantity of heat which would correspond to the total transformation of the first system into the second and q the quantity of heat liberated by mixing the two salts, the expression $\frac{q}{Q}$ gives, with the restrictions already seen, apropos of hydrolysis, the relative proportions of the bodies of the first system, which were transformed into bodies of the second system.

The neutralization of strong acids by strong bases, liberating almost equal quantities of heat, was first shown by Hess. From this it follows that double decompositions of neutral salts of strong acids and bases, stable in the presence of water, do not occasion an appreciable heat effect, even when the transformation is practically

complete. The thermal effects are more important in proportion as the stability of the two salts in the presence of water is more different from what we have seen previously concerning the classification of salts in regard to this stability.

As it is a question here of essentially reversible reactions, in which there is consequently the production of no non-compensated work, the principle of maximum work necessarily does not find any application in double decomposition of salts, and the transformation of one system of two salts into the opposite system is done either with evolution or with absorption of heat. What controls the direction of the transformation is the tendency toward the formation *of the most stable salt in the presence of water,* and also, as an inevitable consequence, to the correlative formation of the least stable salt, more or less hydrolyzed. As the numerous experiments of Berthelot prove, "the strong acids unite by preference with strong bases, leaving the weak bases to the weak acids."* It is, moreover, to be noted that the more stable salt is the one which corresponds to the maximum liberation of heat, but it does not follow that the sign of the heat of the reaction ought necessarily to be positive. One of the most striking examples in this respect is the action of potassium carbonate on ammonium sulphate, whose equimolecular quantities absorb —6.36 Calories. The total transformation into potassium sulphate and ammonium carbonate would correspond to —6.81 Calories. There is, then, more than nine tenths of the system transformed, although the reaction is strongly endothermic.

Experiments show that the transformation is often much more complete when one of the bodies can be eliminated in the form of an insoluble precipitate or a volatile compound, without, however, this physical property being the *determining* cause of the transformation, for, in a great many cases, it takes place in the inverse direction. For example, in the reaction:

$$PbSO_4 + 2NaC_2H_3O_2 = Na_2SO_4 + Pb(C_2H_3O_2)_2,$$

it is the insoluble lead sulphate that is dissolved by the sodium acetate, and, in the still more numerous cases of insoluble bodies, carbonates, phosphates, etc., being acted upon by strong acids. These reactions are used frequently in analytical chemistry. However, we will see further, as an application of the numerical law of equilib-

* *Loc. cit.,* II, p. 712.

rium that every time it is possible, insolubility or volatility plays a very important part in accentuating the direction of the transformation.

Equilibrium in double decomposition of salts, is attained in general with great rapidity, as is shown by the reactions effected in the calorimeter where the maximum or minimum temperature is attained in a few seconds. This is true for reactions in which all the bodies remain soluble, and, for a great number of double decompositions giving crystalline precipitates. For example, in the action of sulphuric acid on barium chloride, of ammonium oxalate on soluble salts of calcium, etc., and, if, in other cases, we allow the precipitate to digest in the hot mother liquor, it is less to complete the precipitate than to increase the size of the grains and to facilitate the filtration (see Chapters I and II). If, in certain cases of simple double decompositions (consisting in the pure and simple exchange of bases and acids), we are obliged to wait some time for the appearance of the expected precipitate or for the precipitation to become complete, that depends upon the fact that the insoluble precipitate begins by being more soluble, whether on account of its minute state of division, and that its supersaturation must be completely destroyed in order that the equilibrium be established, or because it forms first in the colloidal state, giving a pseudo-solution which requires a certain time of contact with the salts or acids in solution in order to be precipitated. It is especially true that retardation of the formation of the precipitates occurs in precipitations taking place in extremely dilute solutions (precipitation of traces of sulphuric acid by $BaCl_2$, of traces of calcium by ammonium oxalate, of metals in extremely dilute solutions by hydrogen sulphide which gives colloidal sulphur).

When the double decomposition is not simple and produces salts formed of acid radicals or complex bases, necessitating, as a consequence, an intermediate reaction of decomposition and, of recombination of the elements of the bodies of the first system, the limit is often much longer in being attained. Such is the case in the formation of magnesium ammonium phosphate from ammonium phosphate and magnesium chloride, of potassium chlorplatinate by the action of potassium chloride on platinic chloride, of potassium cobaltonitrite by the action of potassium nitrite on cobalt salts, etc.

But, taking these particular facts into account, and with the same restrictions as for the phenomena of hydrolysis, in that which

concerns the possible modifications in the chemical function of precipitates, the reversibility of the phenomena of double decomposition in proportion to concentration and temperature, is placed beyond doubt, as a general rule, by the multitude of experiments and numerous examples which will be given later.

2. Experimental Research upon the Numerical Law of Equilibrium in Double Decompositions

We have just seen how, by the conception of the hydrolysis of salts in aqueous solutions, one may conceive the exchange of acids and of bases in the mixture of two salts. The calorimeter taught us that these reactions are not generally complete and that they cause equilibrium between bodies of two opposed systems; even, in certain cases, it permits the determination of the state of equilibrium of the system when it is a question of almost instantaneous reactions. But, in order that the data furnished by the calorimeter may be utilized in ascertaining the conditions to be fulfilled in view of the practically total precipitation of insoluble bodies, it is necessary that we have precise conceptions concerning the influence of the factors of equilibrium, namely; the temperature t and the concentration c, of the reacting bodies. The other factors such as the pressure, electric state, etc., remain generally constant and are not able, consequently, to vary the state of equilibrium of the system.

The mathematical law $f\ (c,\ c',\ c''\ \ldots\ .\ .\ .\ t) = 0$, which governs the equilibrium in double decomposition, has engrossed the minds of chemists for more than a century. It is by a series of successive trials and improvements that it has been established, at first experimentally, then in a theoretical manner, by basing it upon the principles of thermodynamics, and thus bringing it in a form which is probably only one stage toward the exact solution, but which appears already sufficiently near, as we shall see, for operations of a practical character like those of analytical chemistry.

Historical.—Bergmann is the first chemist who occupied himself with explaining the mechanism of double decomposition in building up his general theory of affinities, founded upon the mutual "attraction" of bodies. His theory may be summarized as follows: All bodies exercise an attraction upon each other, the magnitude of this attraction can be expressed by a definite number. Different bodies have different attractions for the same body. If the body A has a greater attraction for the body B than for the body C, the body B will drive the body C from its combination with A or,

$$AC+B = AB+C.$$

It is upon this hypothesis as a foundation that Bergmann established in 1775 his celebrated *Table of Affinity*. In Bergmann's theory, insolubility, volatility, and the relative concentration of the reacting bodies have no influence upon the chemical reaction.

This theory contained manifest errors, and, in 1801 to 1803, Berthollet developed a theory of affinity, in a contrary direction to that of Bergmann, in the *Annales de Chimie* and in *l'Essai de statique chimique*. This theory rests upon the following principles: According to Berthollet, all bodies have an affinity for each other, but this affinity varies, according to the bodies under consideration, and depends essentially upon the physical properties of the combination which they can produce; *cohesion* (insolubility), and *volatility* (elastic force of the gases resulting from the reaction). Bodies can react upon each other only if their smallest particles are in close contact, for example, in solution. The chemical action of bodies depends upon the affinities and quantities of the two bodies; a body is withdrawn from chemical action each time that it is precipitated in an insoluble form, or when it takes the gaseous form.

Berthollet did not fall into the error, with which he is wrongfully blamed, of believing that insolubility suffices to determine the direction of the reaction, for he has called attention to the fact that it can be produced in inverse order. Take, for example, the insoluble salts of calcium; "oxalic acid," said Berthollet,* "precipitates as calcium oxalate only a part of the calcium which forms a neutral combination with another acid. As soon as the acid of the combination has acquired a certain energy by the diminution of the base, it counterbalances the effort of insolubility, and the calcium oxalate ceases to separate. Again, the insolubility of the phosphate or the sulphate of calcium is overcome much more readily; a weak acidity suffices to make the effect disappear."

One cannot define more clearly a state of equilibrium between two reversible reactions, dependent upon the concentration of the bodies in solution. But Berthollet's attention being doubtless turned toward practically complete reactions, with insoluble precipitates or with volatile products, he has not made any direct measurement of the partition of the base between two acids in solution. He contented himself with admitting without proof that this partition takes place in all cases, proportionally to the reacting masses of the

* Berthollet, *Essai de statique chimique*, I, p. 78.

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acids (when, in fact it is produced according to an entirely different law, as we shall see), and this error cast for a long time unmerited discredit upon his very correct conception of the equilibrium between the two opposed states of a double decomposition.

It is barely half a century after the work of Berthollet that the study of the law of this equilibrium was resumed. This study at the very first bore upon the verification of the existence of a common limit between the two opposed states of the system and upon the determination of this limit. Malaguti* investigated a great number of double decompositions by pouring the mixture of the solutions of two salts into a large excess of alcohol. In all cases where two of the four salts produced by the mutual reaction are insoluble in alcohol, the analysis of the precipitate permits the easy determination of the proportion of the salts of the first system changed into those of the opposed system, if we admit that the addition of alcohol does not modify the repartition of the acids among the bases and that the precipitate well represents the state of the combinations in the aqueous solution. This last point is rather questionable, *a priori*, however the experiments of Malaguti seem, indeed, to justify this hypothesis, the coefficient of partition having been found to be the same when starting from the two opposed systems, as is shown by the following results obtained by this author:

Reacting Substances Mixed (One Equivalent of Each Salt)	Composition After Precipitation by Alcohol	Coefficient of Partition
Lead Nitrate	0.92 Potassium Nitrate and Lead Acetate	0.91 to 0.92
Potassium Acetate....	0.08 Lead Nitrate and Potassium Acetate	
Lead Acetate.....	0.91 Potassium Nitrate and Lead Acetate	
Potassium Nitrate...	0.09 Lead Nitrate and Potassium Acetate	
Zinc Sulphate.....	0.84 Potassium Sulphate and Zinc Chloride	0.83 to 0.84
Potassium Chloride..	0.16 Zinc Sulphate and Potassium Chloride	
Potassium Sulphate..	0.83 Potassium Sulphate and Zinc Chloride	
Zinc Chloride.....	0.17 Zinc Sulphate and Potassium Chloride	

* Malaguti, *Ann. Chim. Phys.*, (3) xxxvii, 198 (1853).

Starting from either of the two opposing systems, the limits reached are the same.

The study of the esterification of alcohols by acids, comparable to the double decomposition of salts, undertaken from 1860 to 1863 by Berthelot and Péan de Saint-Gilles* enables one to obtain in a very clear manner the limits corresponding to the equilibrium. This limit is almost independent of the temperature, but is attained very slowly in the cold. It is reached in a few hours at 200°. With acetic acid and alcohol, there is obtained, as a limit, 67.3 per cent of ethyl acetate at the end of twenty-eight hours at 200°, and, in starting with the opposite system, ester and water, 69.3 per cent undecomposed ester is obtained.

In his researches, Malaguti occupied himself especially with verifying the existence of a limit and in measuring it by employing equivalent mixtures. This method gives no information concerning the influence of the reacting masses upon the final state of equilibrium and, in order to obtain this, it would have been necessary to vary successively the masses of the reacting substances contained in unit volume, that is, their concentration. In these experiments, Berthelot and Péan de Saint-Gilles observed carefully what occurs when an equivalent of acid is mixed with several different equivalents of alcohol, and reciprocally. But the very simple result at which they arrived in these special reactions, namely: the proportionality of the quantity of the ester produced, first to the quantity of the alcohol employed, and, second, to the quantity of the acid, had hidden from them the exact expression of the mathematical relation of the phenomenon, which, in this case, is particularly complicated, because the ester produced is not soluble in water which dissolves only the alcohol and the acid, and because, consequently, one does not deal with a homogeneous liquid system.

Work of Guldberg and Waage.—A short time after the researches of Berthelot and Péan de Saint-Gilles on esterification, two Norwegian scholars, C. M. Guldberg and P. Waage presented in a memoir, entitled *Études sur les affinités chimiques,* published in French in Christiana in 1867 the results of their researches upon the double decomposition between barium sulphate and potassium carbonate limited by the reverse action of potassium sulphate upon the barium carbonate produced, as the previous experiments of

* Berthelot and Péan de Saint-Gilles, *Ann. Chim. Phys.,* (3) lxv, 385 (1862); (3) lxvi, 5, 111 (1862); (3) lxviii, 225 (1863).

Dulong and of H. Rose had proved. In their investigation, Guldberg and Waage studied with the greatest care the influence of concentration and of temperature upon equilibrium as well as the speed of reaction and the influence of foreign bodies added to the system. They also investigated equally thoroughly the speed of evolution of hydrogen in the action of acids on metals. The conclusions of their researches are that, in a double decomposition, limited by a reverse reaction, the force which produces the transformation of the system, of the bodies A+B into a system of bodies A′+B′ is *proportional to the product of the active masses of the two bodies A and B,* and to a certain *coefficient of affinity* peculiar to the reaction $A+B = A'+B'$. If p and q represent the active masses of the bodies A and B in unit volume, the force in question is equal to $k \cdot p \cdot q$.

If we call p' and q' the active masses of A′ and B′, and k' the coefficient of affinity peculiar to the reverse reaction

$$A'+B' = A+B,$$

we will have, likewise, for the force which produces the transformation, the value $k' \cdot p' \cdot q'$.

If, then, the temperature being constant, we consider the moment when the equilibrium is established, the two opposing forces ought to be equal and consequently we should have:

$$k \cdot p \cdot q = k' \cdot p' \cdot q'. \qquad (1)$$

By determining the active masses p, q, p' and q' by direct experiment, we can find the ratio between the coefficients k and k' and prove that this ratio is constant, by varying the initial masses of the reacting bodies:

$$BaSO_4 + K_2CO_3 \leftrightarrow BaCO_3 + K_2SO_4.$$

If we designate by P, Q, P′ and Q′ the absolute initial quantities of the four bodies A, B, A′ and B′ before the reaction; by x, the number of molecules of A and B that are transformed into A′ and B′; and by V, the total constant volume of the solution; we will have:

$$p = \frac{P-x}{V}, \quad q = \frac{Q-x}{V}, \quad p' = \frac{P'+x}{V}, \quad q' = \frac{Q'+x}{V}.$$

By introducing these values into equation (1) and multiplying by V^2, we obtain:

$$(2) \qquad (P-x)\,(Q-x) = \frac{k'}{k}\,(P'+x)\,(Q'+x).$$

If we suppose with the authors that the active masses of the insoluble or very slightly soluble bodies A (barium sulphate) and A′ (barium carbonate) remain constant, at least approximately, which is justifiable, since the solution being always necessarily saturated to these bodies, their concentration in the solution is constant, the equation (2) is reduced, p and p' being constant, to

$$(3) \qquad Q-x = \frac{k'}{k}(Q'+x),$$

from which we derive:

$$(4) \qquad x = \frac{Q-\frac{k'}{k}Q'}{1+\frac{k'}{k}}$$

and

$$(5) \qquad \frac{k'}{k} = \frac{Q-x}{Q'+x}.$$

$\frac{Q-x}{V}$ being the concentration, $C_{K_2CO_3}$ of potassium carbonate, and $Q'+x$ the concentration, $C_{K_2SO_4}$, of potassium sulphate, the mathematical law to which Guldberg and Waage arrived amounts to the expression:

$$\frac{C_{K_2SO_4}}{C_{K_2CO_3}} = \frac{k'}{k} = C \text{ (constant)}.$$

In general, if we call C and C′ the concentrations respectively of the bodies A and B, of the first system, C″ and C‴ that of the bodies A′ and B′, of the secondary system, equation (2) takes the form:

$$\frac{C\cdot C'}{C''\cdot C'''} = \frac{k'}{k} = \text{Constant}.$$

In the reaction studied, the value $\frac{k'}{k}$ for a particular experiment was found to have a value of 4. The experiments were made at 100° and since boiling water dissolves glass, silver or platinum flasks were employed. Into these flasks pure barium sulphate was introduced, then solutions of different concentration of either potassium carbonate or potassium carbonate and potassium sulphate. It

was sufficient to determine the sulphuric acid in the liquid and the carbonate of barium in the insoluble residue, when the equilibrium was established, in order to deduce the number of molecules, x transformed. The following table compiled by the authors, gives the values of x, which were on the one hand observed and on the other calculated by formula (4), taking $\frac{k'}{k} = 4$, for the different values of Q and Q′, (expressed in molecules of salt dissolved in 500 molecules of water):

Q	Q′	x Observed	x Calculated
2.0	0	0.395	0.400
2.5	0	0.500	0.500
3.5	0	0.719	0.700
2.5	0.25	0.300	0.300
3.0	0.25	0.408	0.400
2.0	0.50	0.005	0.000

The agreement between the calculated and observed values of x is very satisfactory, but the authors, in order to compile this table, have employed only the figures corresponding to concentrations which are but very slightly different.

From the experimental results of Guldberg and Waage, which represent wider ranges of concentrations, Van't Hoff* obtained the following table which shows less satisfactory agreement:

Q	Q′	x Observed	$\frac{Q-x}{Q'+x}$ Calculated
3.5	0	0.719	3.87
2.5	0	0.500	4.00
2.0	0	0.395	4.07
1.0	0	0.176	4.68
2.0	0.25	0.200	4.00
2.5	0.25	0.300	4.00
3.0	0.25	0.408	3.94
3.8	0.25	0.593	3.80
2.0	0.50	0	4.00

The extreme values of the ratio of the coefficients of affinity, 3.80 and 4.68, represent a difference of 12 per cent of the average ratio. This difference is certainly greater than the experimental errors because the studies made by Guldberg and Waage, upon the

* Van't Hoff, memoir on the *Lois de l'équilibre chimique dans l'état dilué gazeus ou dissous,* Stockholm, p. 30, 1886.

speed of reaction show that with a very close approximation, the limit is attained in general, at the end of three or four days. As an example,—one of the diagrams published in their paper is reproduced (Figure II). The curve represents diagrammatically the results obtained at 100°, when one molecule of barium sulphate was acted upon by one molecule of potassium carbonate dissolved respectively in 67.67 molecules of water, curve 1; 100 molecules of water, curve 2; 500 molecules of water, curve 3; 1,000 molecules of water, curve 4. The abscissas represent the time and the ordinates the values of x (the percentage of the insoluble body decomposed).

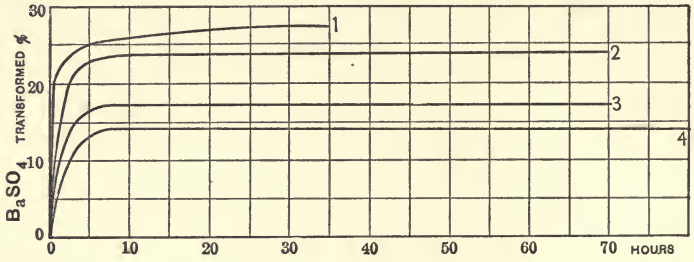

FIG. II

The study of the form of these curves shows that they can be represented by an equation of the form

$$\frac{dx}{dt} = k(\xi - x),$$

where x represents the quantity of the insoluble body transformed at the end of the time t, ξ the limit of the transformation, and k a constant depending upon the concentration. The regularity of these curves and definiteness of the position of the asymptote $x = \xi$ are such that one must necessarily attribute the differences between the values of the ratio $\frac{k'}{k}$ to the fact that the law of equilibrium, deduced by Guldberg and Waage, from their experiments, is not entirely exact.

Although still imperfect and teaching nothing concerning the variation of the coefficient $\frac{k'}{k}$ with the temperature, the law of Guldberg and Waage, nevertheless, marked a very important step in the discovery of the law of equilibrium in double decompositions,

in that it stimulated careful investigation, by means of which the more exact form, deduced from the principles of Thermodynamics, could be submitted to numerous experimental verifications.

Very soon Guldberg and Waage, themselves, perceived, after the publication of their paper in 1867, that the general law which they had formulated, $\frac{C \cdot C'}{C'' \cdot C'''} = C(\text{constant})$, should be modified by introducing an exponent, indicating for each concentration, the number of molecules taking part in the reaction. Then, if the reaction is represented by the equation $n\text{A} + n'\text{B} \leftrightarrow n''\text{A}_1 + n'''\text{B}_1$, the mathematical expression of the equilibrium is

$$\frac{C^{n} \cdot C'^{n'}}{C''^{n''} \cdot C''^{n'''}} = C \text{ (constant)}^*$$

an equation in which all of the exponents reduce to unity in the fundamental reaction of their theory:

$$BaSO_4 + K_2CO_3 \leftrightarrow BaCO_3 + K_2SO_4,$$

in which only one molecule of each of the substances is involved.

Verifications of the Law of Guldberg and Waage.—It is toward the verification of the final equation of Guldberg and Waage that the later investigations have been directed with different degrees of success, the experiments giving at times perfect verification and again, on the contrary, flagrant disagreements.

One of the first researches undertaken with this object in view, was the investigations of Thomsen on the equilibrium which is established by adding sulphuric acid to a dilute solution of sodium nitrate: $H_2SO_4 + NaNO_3 \leftrightarrow NaHSO_4 + HNO_3$, a reaction whose limit of transformation is easily determined by the calorimeter and the results are in perfect accord with the law of Guldberg and Waage.†

On the other hand, the studies made shortly after, in 1872, by Schloesing‡ upon the transformation of insoluble alkaline earth carbonates into bicarbonates, gave results in complete disagreement with the equation of Guldberg and Waage. In the reaction,

* *Jour. prakt. Chem.*, (2) xix, 69 (1879).

† Thomsen, *Thermochemische Unterschungen I.*

‡ Schloesing, *C. R.*, lxxiv, 1552 (1872) and lxxv, 70 (1872).

$$BaCO_3 + CO_2 \text{ (dissolved)} \leftrightarrow Ba(HCO_3)_2$$

the above mentioned equation would give

$$\frac{C_{CO_2}}{C_{Ba(HCO_3)_2}} = C \text{ (constant)}$$

or, $x = k \cdot y$, where x represents the pressure of the carbon dioxide proportional to its concentration, y, the quantity of carbonate dissolved in a definite volume of water, and k, a constant. Schloesing showed that the phenomenon follows an entirely different law represented by the equations:

$x^{0.38045} = k \cdot y$ for the barium carbonate;
$x^{0.37866} = k \cdot y$ for calcium carbonate.

There exists then, a deficiency in the mathematical law of Guldberg and Waage. It could only be supplied by the application of the principles of Thermodynamics to the reversible phenomena of chemistry. The first attempt to do this has been made almost simultaneously by Moutier and Peslin in France, and by Horstmann in Germany, who were to pave the way later for Van't Hoff and Le Chatelier to complete the equation of Guldberg and Waage by terms which experiment alone had been powerless to reveal.

3. Analogous Law Drawn from the Principles of Thermodynamics

Equation of Van't Hoff and H. Le Chatelier.—J. H. Van't Hoff, in his memoir on the *Laws of Chemical Equilibrium in the Dilute State, Gaseous and in Solution,* presented to the Royal Academy of Sciences of Sweden, October 14, 1885*, gave a mathematical expression of the law controlling equilibrium in double decompositions, completing the equation of Guldberg and Waage by the introduction of a temperature factor. Without entering into the details of the calculations, we will only indicate the course pursued by him.

The starting point of Van't Hoff is the law of Osmotic Pressure,

$$\Pi V i = iRT$$

* A Memoir printed in French in 1886 at Stockholm (Royal Printing Office) and in the *Archives Néerlandaises,* Vol. 20.

for bodies in aqueous solution, combined with the law of Mariotte-Gay Lussac,

$$PV = RT$$

for molecular weights of gases. In the first formula Π represents the osmotic pressure of the dissolved salt molecules, i is a constant coefficient, peculiar to every dissolved substance, deduced from the experiment of Pfeffer and de Vries to which we will return subsequently, R, a constant equal to 845, expressed in meter-kilogram units.

Van't Hoff makes use of the conception of the semipermeable membrane, used by Pfeffer for the measurement of osmotic pressure, and conceives a dilute solution as describing a series of cyclic reversible transformations, first at a constant temperature and then at a variable temperature. He thus arrives, basing his conception upon the principle of Carnot-Clausius, at the following equations:

$$(1) \qquad \frac{C^{\Sigma ni}}{C_1{}^{\Sigma n_1 i_1}} = k = C \text{ (constant)}$$

for an isothermal transformation and

$$(2) \qquad \frac{d \log k}{dT} = \frac{q}{ART^2}$$

for a transformation at a variable temperature.

In these equations C represents the concentration of the substances in the initial system, when the equilibrium is established, C_1 the concentrations of the substances of the second system; n, n_1, the number of molecules participating in the reaction; i, i_1, the coefficients of the law of osmotic pressures specific for each of the substances of the two systems; A is the reciprocal of the mechanical equivalent of heat; finally, q represents the heat liberated by the transformation of n_1, n'_1, molecules of the second system into n, n', molecules of the first.

Shortly after the publication of Van't Hoff's memoir, Le Chatelier gave a different demonstration of the same mathematical law in his memoir, entitled *Experimental and Theoretical Researches on Chemical Equilibrium*, published in 1888.* The starting point of

*H. Le Chatelier, *Ann. des Mines*, (8) xiii, 157-382 (1888).

this demonstration is the formula of Clapeyron-Clausius, upon the laws of the pressure of saturated vapors applied to the phenomena of simple dissociation of heterogeneous systems (calcium carbonate, for example). This law is extended to the phenomena of the dissolution of gases in water with the help of Henry's Law: $P = kC^i$ at constant temperature, then to the dissociation of homogeneous systems, finally, on the assumption that all substances are volatile, to saturated solutions, and finally to double decomposition of salts. The form of the law thus reached by Le Chatelier is expressed as follows:*

$$\log \frac{C^{ni}C'^{n'i'}}{C''^{n''i''}C'''^{n'''i'''}} + \frac{I}{AR}\int \frac{L dT}{T^2} = C \text{ (constant)}$$

in which the terms C, n, A, R, and T have the same significance as in Van't Hoff's equation. The coefficients i, however, are those obtained by the cryoscopic measurements of Raoult (identical with those given by the osmotic pressure method). Finally, L is the heat liberated in the transformation of n, n' molecules of the first system into n'', n''', molecules of the second system (that is to say, equal to the terms of Van't Hoff's equation with the sign reversed).

The equations of Van't Hoff and of Le Chatelier are then identical. Both are established for very dilute solutions and assume that Mariotte's law or the law of osmotic pressure holds without change of coefficient in all the changes of concentration studied. Besides, the amount of the solvent is supposed to remain constant and does not, therefore, explicitly appear in the equation. Insoluble substances, whose concentration may be regarded as constant, do not enter either into the equation, which is the same thing as considering their volume in the solid state negligible in comparison to their volume occupied in the gaseous state. However, although this law is only approximate, we will see that it is verified experimentally up to higher concentrations than one has to use in analytical chemistry.

L being, in general an unknown function of the temperature, we cannot integrate the term $\int \frac{L dT}{T^2}$ but, inasmuch as only reactions occurring at a definite temperature need to be considered in analytical chemistry, it is not necessary to know the form of this function in order to discuss the equation and deduce from it the most favor-

*H. Le Chatelier had previously given *C. R.*, ci, 1484 (1885), the same equation for equilibrium in gaseous systems.

able conditions in analysis, and we can content ourselves in general with the equation reduced to the case of *isothermal* transformations:

$$\frac{C^{ni}C'^{n'i'}}{C''^{n''i''}C'''^{n'''i'''}} = C \text{ (constant)}$$

the value of the term under the $\int$ sign remaining constant in such transformations.

Experimental Verification of the Approximate Law of Equilibrium in Double Isothermal Decompositions.—The law of Guldberg and Waage differs, definitely, from the preceding expression only in the coefficients *i*. It can then be understood that, according as these coefficients are but slightly different from each other or, on the contrary, very different, excellent agreement or considerable variation has been obtained between the data of the experiments and the results calculated by means of the Guldberg-Waage equation.

Let us take up again the experiment previously considered. In the reaction

$$BaSO_4 + K_2CO_3 \leftrightarrow BaCO_3 + K_2SO_4$$

the coefficients *i* are almost equal, 2.26 for K_2CO_3 and 2.11 for K_2SO_4, so that Van't Hoff's equation becomes

$$\frac{C_{K_2CO_3}^{2.26}}{C_{K_2SO_4}^{2.11}} = \frac{C_{K_2CO_3}^{1.07}}{C_{K_2SO_4}} = C \text{ (constant)}$$

an equation differing but little from that of Guldberg and Waage. In calculating again by means of this corrected equation the constant of the table compiled by Van't Hoff from the data of the experiments of Guldberg and Waage, we obtain a much more satisfactory agreement between the experimental and the calculated values as shown by the accompanying table.

Q	Q′	x	$\frac{Q-x}{Q_1+x}$	$\frac{(Q-x)^{1.07}}{(Q_1+x)}$
3.5	0	0.719	3.87	4.16
2.5	0	0.500	4.00	4.20
2.0	0	0.395	4.07	4.20
1.0	0	0.176	4.68	4.62
2.0	0.25	0.200	4.00	4.17
2.5	0.25	0.300	4.00	4.23
3.0	0.25	0.408	3.94	4.21
3.8	0.25	0.593	3.80	4.13
2.0	0.50	0.000	4.00	4.20

While the difference between 4.68 and 3.80 is 12 per cent of the average value 4.09, with the formula of Guldberg and Waage, it is only 8 per cent with the extreme values, 4.13 and 4.62, by comparison with the average 4.23, which is given by the thermodynamic equation.

Likewise, we see why the Guldberg and Waage formula may have conformed exactly with the experiments of Thomsen upon the equilibrium:

$$Na_2SO_4 + HNO_3 \leftrightarrow NaHSO_4 + NaNO_3.$$

The values of i are, in fact, almost identical for the substances of the system in equilibrium; 1.91 for Na_2SO_4, 1.94 for HNO_3, 1.88 for $NaHSO_4$ and 1.82 for $NaNO_3$.

On the contrary, the formula of Guldberg and Waage is in complete disagreement with the reaction studied by Schloesing,

$$BaCO_3 + CO_2 \text{ (dissolved)} \leftrightarrow Ba(HCO_3)_2 \text{ (dissolved)}$$

where the coefficients i are very different; 1.0 for CO_2, 2.66 for the bicarbonate of barium and 2.56 for the bicarbonate of calcium.

In this case, Van't Hoff's formula leads to the equations

$$X^{0.376} = ky \text{ for } BaCO_3, \quad X^{0.390} = ky \text{ for } CaCO_3,$$

which is absolutely in accord with the analogous equation previously indicated, and deduced from the experimental data.

Other verifications of the thermodynamic law have been made and the agreement has always been satisfactory. We will content ourselves by giving here the following two experimental verifications which relate more especially to cases frequently considered in analytical chemistry:

(1) *The experiment of Ostwald upon the decomposition of zinc sulphide by sulphuric acid.**

In the reaction of equilibrium,

$$H_2SO_4 + ZnS \leftrightarrow ZnSO_4 + H_2S,$$

the thermodynamic equation, replacing i by its corresponding values and taking into account the fact that the sulphide of zinc is insoluble, becomes,

* Ostwald, *Jour. prakt. Chem.*, (2) xix, 480 (1879).

$$\frac{C_{H_2SO_4}^{2.06}}{C_{ZnSO_4}^{0.98} \cdot C_{H_2S}^{1.04}} = C \text{ (constant)}.$$

As in the initial system, there is neither sulphate of zinc nor hydrogen sulphide, the concentrations of these two substances are necessarily equal and the equation reduces to

$$\frac{C_{H_2SO_4}^{2.06}}{C_{H_2S}^{2.02}} = C \text{ (constant)}.$$

Here is the comparison of the observed and calculated values of one of the experiments which was taken as a basis in the calculation of the constant:

H_2SO_4 C (Observed)	H_2S	
	C Observed	C Calculated
0.250	0.595	0.600
0.125	0.296	0.300
0.062	0.150 (poor)	
0.031	0.077	0.075

The agreement is absolute.

(2) *Experiments of Le Chatelier upon the hydrolysis of mercuric sulphate.*

In the reaction studied,

$$3HgSO_4 + 2H_2O \leftrightarrow HgSO_4 \cdot 2HgO + 2H_2SO_4$$

i is equal to 0.98 for $HgSO_4$ and to 2.06 for H_2SO_4, the basic sulphate is insoluble and the concentration of water is assumed to be constant. The equation of the isothermic equilibrium then gives,

$$\frac{C_{H_2SO_4}^{2.94}}{C_{H_2SO_4}^{4.12}} = k \text{ or } C_{H_2SO_4}^{1.40} = k\, C_{HgSO_4}.$$

Here is the table of comparison between the experimental and calculated values, compiled from this author's data obtained at 13°.

$HgSO_4$ Number of Equivalents in 10 Liters	H_2SO_4 Number of Equivalents in 10 Liters	
	C Observed	C Calculated
3.18	7.52	6.33
3.88	8.80	7.29
4.70	9.70	8.36
5.92	11.50	9.86
8.90	14.20	13.20
12.90	17.20 (poor)	
13.00	17.50	17.29
18.00	21.00	21.82
20.20	24.00	23.70

The agreement is satisfactory, for the result of the experiments may be represented by the equation:

$$C^{1.58}_{H_2SO_4} = k\ C_{HgSO_4}$$

instead of

$$C^{1.40}_{HgSO_4} = k\ C_{H_2SO_4}$$

which is given by the thermodynamic formula.

We can, then, in fact, consider the equation of Guldberg and Waage corrected by the introduction of the coefficient i, as a theoretical and experimental law of the equilibrium in double decompositions of salts and sufficiently exact for its application to chemical analysis, where it is a question especially of determining the direction in which the reaction should proceed in order to make it as complete as possible. As experience has already indicated for each method the approximate degree of precision of which it is capable, it is unnecessary, in general, to repeat for each complete study of the equilibrium as in the examples just given, and we can content ourselves with verifying whether the method of operation conforms to the deductions which can be drawn from the general law of equilibrium or if we should, on the contrary, make it undergo changes according to these deductions. In this respect, it is not even necessary to know accurately the constant of the law of equilibrium in each particular case, nor the coefficient i in order to be able to take into account the manner in which the temperature and concentration influence the direction of the double chemical decomposition under consideration, which often suffices to interpret

a definite method of chemical analysis. The principle of Le Chatelier in consequence of the displacement of the equilibrium under the influence of the variation of one of the above factors or *the law of opposition of reaction to action** (which is deduced either from the experimental study of reversible reactions, or from the preceding general equation in varying successively each factor) is usually sufficient in the discussions in analytical chemistry. We will recall in view of the applications we will have to make of it that, for double decompositions of salts, this principle can be expressed thus: if the reaction liberates heat, an elevation of the temperature should diminish the transformation of the first system into the second and inversely, the increase of concentration of one of the substances of the first system increases the transformation of this system into the second and inversely.

Significance of the Laws of Berthollet.—As a conclusion to this calorimetric study of the double decomposition of salts and at the same time as an immediate consequence of the Guldberg-Waage law, we should see what is the exact rôle of the physical characteristics, the *insolubility* and the *volatility*, of substances which can be produced in a double decomposition of salts, that is to say, to examine the scientific value of the laws of Berthollet.

Let us assume, in the equilibrium reaction

$$A+B \leftrightarrow A_1+B_1$$

that the factors n are equal; and likewise, the coefficients i; this does not change anything in the reasoning we are going to follow and has for its object the simplification of the discussion.† Let us consider the case of an isothermal transformation of two substances constantly of the same concentration (with the same number of equivalents). The general equilibrium equation reduces to:

$$\frac{C \cdot C}{C'' \cdot C''} = C \text{ (constant) or } \frac{C}{C''} = k.$$

That is to say, the proportion of the first system transformed into the second is the same whatever may be the initial concentration, on the condition, of course, that all the substances present remain in the solution in the dissolved condition.

* Le Chatelier, *Ann. des Mines, Series* (8), Vol. 13.

† This discussion is taken from the previously cited memoir of Le Chatelier.

But, let us now assume that one of the substances of the second system, B_1, for example, attains its limit of solubility and begins to precipitate. From this moment, its concentration s becomes constant. The preceding equality becomes

$$\frac{C \cdot C}{C'' \cdot s} = k, \text{ or } \frac{C}{C''} = \frac{ks}{C}.$$

That is to say that, if we continue to increase simultaneously the concentration of the substances of the first system, the ratio $\frac{C}{C''}$ which was constant until then, is going to diminish suddenly from the moment the substance B_1 begins to precipitate, since ks is constant and C increases. This signifies that C″ is going to increase proportionally more rapidly than C, consequently, the precipitation of the substance B_1 correlative to the formation of the substance A_1, is going to continue increasing and it can be practically complete if s is sufficiently small and k is not too large.

This is the explanation of the laws of Berthollet; the *insolubility* of substances is not the reason for the reactions in double decomposition of salts, but it makes them practically complete when k has a very small value. The same is true for the *volatility* of the substance.

But, if k is very large, while s is very small, we see that the precipitate cannot be produced, since the transformation of the first system into the second may be very slight. This explains, for example, the lack of action of carbon dioxide upon calcium chloride, in spite of the insolubility of calcium carbonate, as well as the numerous exceptions to the law of Berthollet, when it is a question no longer of the action of salts upon salts, but of acids and bases upon salts. This comes from the fact that in this case the coefficient k is quite large, and, consequently, the product ks may take a large value notwithstanding the small value of s.

What makes the Berthollet laws really applicable in many cases, is that frequently the coefficient k, whose magnitude depends upon that of the heat of reaction L, takes finite values approaching unity, when L is zero, a condition realized in the simple double decomposition of all salts formed by a strong acid and a strong base (alkali and alkaline earths, salts of sulphuric, hydrochloric and nitric acids) and which led the chemist Hess to formulate the law of thermoneutrality.

In the action of acids on salts, the heat of displacement of the

medium or weak acids by strong acids attains much more important values. Thus, in some cases the laws of Berthollet often seem at fault whereas they should be utilized only when the heat of neutralization of the same base by two acids is practically the same; likewise, for the action of bases upon salts.*

From the form of the mathematical law of equilibrium in double decompositions of salts, it is apparent that the influence of variations of temperature upon the coefficient of partition k is small when the heat of reaction L is very small, that is to say, in the cases where the law of Berthollet is applicable. Temperature can, however, in certain cases of analysis, play an important rôle by modifying the solubility of the reacting substances and also of the products of the reaction. It may happen, in fact, according as one employs a cold or a hot solution, that it is a salt of the one or of the other system that first reaches its limit of solubility, so that the direction which the reaction tends to take in order to become more complete, may be reversed by a variation of the temperature. This is one of the reasons why the temperature employed in analytical chemistry at which each precipitation should be produced, ought to be very carefully determined.

A special difficulty presents itself in this respect, which at times is impossible to overcome. Since most all salts are more soluble in hot than in cold water it is, in general, preferable to carry on the double decompositions in the cold, so that they may be more complete. But, on the other hand, many precipitates obtained in the cold are too fine or colloidal to be washed and filtered with convenience, and it is of advantage to produce the precipitation from hot solutions in order to increase the size of the grain or to render the precipitate less gelatinous. This is the method by which one may avoid this particular difficulty.

Precipitates, the solubility of which in hot solutions is even very slight, should be produced in hot solutions and then heated near the boiling temperature for some time before filtering (silver chloride, calcium oxalate, barium sulphate, etc.).

Those precipitates are produced in the cold and filtered cold

* Berthollet understood this perfectly and he, himself, indicated the fact that estimates drawn from the physical properties of substances apply only when they are in double decompositions between neutral salts (salts with strong acids and bases), or in the neutral displacement of the acids and bases of the same strength.

whose solubility is excessive when hot, and which are susceptible of assuming rather large crystalline grains when digested in the cold mother liquor (magnesium ammonium phosphate, potassium fluosilicate, potassium chlorplatinate, separation of alkaline earth metals by the insolubility of the nitrates of barium and of calcium in absolute alcohol, etc.).

Finally, in cases in which the grains become rather large only when warmed and where the solubility of the precipitate is too great, heat to incipient boiling and produce the precipitation while hot. Although it is incomplete, rather large crystalline grains are formed and the precipitation is then allowed to finish slowly in the cold. The texture of the precipitate thus formed in the cold is always less fine than when the whole operation is carried out in the cold (precipitation of ammonium phosphomolybdate, of numerous metallic sulphides by hydrogen sulphide, etc.).

CHAPTER IV

THE ELECTROLYTIC THEORY OF DOUBLE DECOMPOSITION OF SALTS

1. Law of Osmotic Pressure

The basis of the electrolytic theory of salt solutions applied by Ostwald to the methods of analytical chemistry is, in the first place, the discovery by Van't Hoff in 1885, of *the law of osmotic pressure,* and, in the second place, the explanation which Arrhenius gave in 1887-1888, of the anomalies, presented by salts in comparison to organic substances, in the values of the osmotic pressures, freezing points and boiling point measurements.

We will recall briefly the experimental work upon which the electrolytic theory rests before we explain the applications made of it by Arrhenius and Ostwald to double decomposition of salts.

Experiments of Pfeffer and of De Vries: Van't Hoff's Law:— The walls of vegetable cells and certain colloidal substances such as copper ferrocyanide, have the property of being penetrated by pure water, but not by the substances dissolved in the water. We can obtain artificially semipermeable membranes like those of vegetable cells, by producing, as the German botanist Pfeffer* did in 1877, a precipitate of copper ferrocyanide within the walls of a porous cup. If, in such a cup, furnished with a mercury manometer, any aqueous solution whatever is placed, of sugar for example, and if the jar be sealed hermetically and placed in pure water, the mercury of the manometer is slowly pressed back by the pure water entering the cup through the semipermeable membrane and finally attains a certain height P, which remains constant.

The water being able to circulate freely through the walls of the jar in both directions, this pressure P can be attributed only to the presence of the dissolved substance. Pfeffer called it the *osmotic pressure* of the solution.

Van't Hoff collected the results obtained by Pfeffer, who experimented at a constant temperature with solutions of different

* Pfeffer, *Osmotische Untersuchungen,* Leipzig, 1877.

concentrations, and at different temperatures, upon solutions of the same concentration, and ascertained that at a constant temperature, the osmotic pressure is proportional to the concentration C and that with equal concentrations, the osmotic pressure is proportional to the absolute temperature T. This is clearly shown by the following table for solutions of cane sugar and of sodium tartrate in water, according to the results obtained by Pfeffer.

C. Constant T. Variable			T. Constant C. Variable			
					Osmotic Pressure	
Concentration of the dissolved substance (cane sugar) in grams per 100 grams of water	Pressure P Observed (millimeters of Mercury)	Ratio $\frac{P}{C}$	Substances Dissolved	Temperature Centigrade	Observed	Calculated on Supposition that $P=KT$
1.	535	535	Sugar	32°.	544	542
2.	1 016	508		14°.15	510	512
2.74	1 518	554	Sodium	37°.30	983	984
4.00	2 082	521	Tartrate	13°.30	908	907
6.00	3 075	513				

The agreement is very satisfactory considering the extreme difficulty of obtaining Pfeffer's cups perfectly semipermeable.

It follows then from this that the concentration C, of a solution, its osmotic pressure P and its absolute temperature T are related by an equation of the form $P = A \cdot C \cdot T$, where A is a constant.

If we consider the molecular weight m of the substance dissolved in a volume V of the solvent, we will have $C = \frac{m}{V}$, and the above equation becomes:

$$PV = Amt \qquad (1)$$

an equation of the same form as the Mariotte-Gay Lussac law:

$$PV = RT. \qquad (2)$$

Van't Hoff conceived the idea of comparing the value Am of equation (1) obtained for sugar ($m = 342$) with that of the con-

stant R of the Mariotte-Gay Lussac law and ascertained that the value of A*m*, equal to 842 (expressing *m* in kilograms and P in kilograms per square meter), is practically the same as that of the constant P of the Mariotte-Gay Lussac law, equal to 846, expressed in the same units. He believed this at first to be a purely accidental coincidence* but, on pursuing the same verification with other data obtained by Pfeffer, and by another botanist, de Vries, he always obtained the same value for the product A*m*, and was thus led to conclude the identity of equations (1) and (2) and that a molecule of a substance transformed into a vapor under the volume V, or dissolved in a volume V of the solvent, has exactly the same vapor pressure and osmotic pressure.

The great difficulty of obtaining Pfeffer porous cups, really semipermeable, has not permitted much repetition and verification of these experiments. However, the experiments of Ponsot† may be cited, who obtained the following results with very dilute solutions of cane sugar placed in different Pfeffer cups:

$t = 11.8°$, $C = 1.235$ g. per liter, $P = 861$ to 890 mm. of liquid
$t = 11.8°$, $C = 0.6175$ g. per liter, $P = 433$ to 444 mm. of liquid.

With the same cells and solutions of 1.235 grams per liter,

$t = 11.8°$, $P = 890$
$t = 0.8°$, $P = 846$, (P calculated $= 855$).

The agreement is less satisfactory than with Pfeffer's data, especially at a variable temperature, but it is still, however, acceptable.

The constant A*m* is then equal to R for the dilute solutions of organic substances. But, for the metallic salts dissolved in water, the constant of the law of osmotic pressure is not the same, and we must replace the preceding equation (1) by an expression of the form:

$$PV = iRT \qquad (3)$$

i being a constant >1, which depends on the nature of the solution. This anomaly has been shown by means of the isotonic coefficients, obtained by de Vries in the following manner. Fresh cells of certain plants present the semipermeable characteristics to a very high degree. Placed in water they swell, while if they are

*Lecture given by Van't Hoff before the Chemical Society at Paris, (*Revue Scientifique,* First Semester, 1894, page 580).

† Ponsot, *C. R.*, cxxv, 867 (1897).

placed in concentrated salt solutions the protoplasm which fills the cell contracts while losing water, which passes through the wall of the cells. By varying the concentration of the dissolved substance, one can obtain solutions in which the protoplasm neither expands nor contracts, and the limit is very clearly defined for a very small variation of concentration.

De Vries* studied, in this manner, the aqueous solutions of a large number of different substances and called those which were in equilibrium with the liquid of the protoplasm isotonic. By experimenting with cellular tissues offering different osmotic forces, it is clear that one can obtain several series of isotonic liquids. De Vries found the same ratio of concentration in the different series, as is shown in the following table giving for potassium nitrate, sugar and potassium sulphate, on the one hand, (A) the absolute concentration expressed in gram-molecules per liter, on the other hand (B), the ratio between the concentrations by taking that of potassium nitrate as unity in the different series:

Series	A			B		
	KNO_3	Sugar	K_2SO_4	KNO_3	Sugar	K_2SO_4
I	0.12	0.12	0.09	1	1	0.75
II	0.13	0.20	0.10	1	1.54	0.77
III	0.195	0.30	0.15	1	1.54	0.77
IV	0.260	0.40	0.15	1	1.54	0.77

These numbers confirm in an almost exact manner the law of proportionality between the concentrations and the osmotic pressures at constant temperature. We see from the preceding table that the isotonic solutions of potassium nitrate, sugar and potassium sulphate, which have the same osmotic pressure, are more concentrated for sugar than for the salts of potassium. If we admit that the pressure is proportional to the concentration, it follows that one molecule of potassium nitrate, for example, dissolved in a volume V of water, gives an osmotic pressure 1.54 times as great as one molecule of sugar dissolved in the same volume V. If, then, the osmotic pressure of sugar is related to the volume V and to the temperature T by the equation $PV = RT$, that of potassium nitrate will be represented by $PV = 1.54RT$; the coefficient i, in the equa-

*De Vries, *Eine Methode zur Analyse der Turgorkraft* (*Pringsheim's Jahrbücher*), Vol. 14.

tion (3), is then equal to 1.54 for potassium nitrate. It is sufficient, in short, to divide the molecular concentrations of sugar and of the saline substances, giving isotonic solutions, the one by the other, in order to obtain the coefficient i, to be introduced into the equation $PV = iRT$ for these saline substances. The table given hereafter (page 96) gives a certain number of coefficients. It is to be noted that the values of i are quite different, according to the experimenters.

Molecular Lowering of the Freezing Point and Vapor Pressure: Raoult's Laws.—The law of osmotic pressure which, on the whole, has been established directly by only a rather small number of concordant experiments, has especially gained in value and forced itself upon physical chemists as the expression of a general phenomenon through the advantageous explanation which it afforded of the data previously determined in freezing point and boiling point measurements, at the time when Van't Hoff discovered this law.

By studying the freezing points of a large number of solutions so diluted that the first crystals formed by the gradual lowering of the temperature, are formed of the pure solvent, Raoult arrived at the following results: For organic substances, the lowering of the freezing point is independent of the nature of the substance dissolved and of the solvent; it is proportional to the concentration and equal to 0.63° for one molecule dissolved in 100 molecules of the solvent. For saline substances in dilute aqueous solutions, the lowering is proportional to the concentration, but has not the same value as cane sugar taken as the unit. Raoult compiled Cryoscopic tables, giving for a large number of substances the proportional lowering i compared to that of sugar. The assumed molecular weights of all of the substances were taken and dissolved in 100 grams of water. If we call Δ the lowering produced by a solution of a salt, we have

$$i = \frac{\Delta}{18.3},$$

18.3 being the lowering produced by sugar. Now, the coefficients i, thus obtained, are practically equal to those that we deduced from isotonic coefficients, as is shown by the following table:

Substance Dissolved	*i* Obtained From the Isotonic Coefficients		*i* Obtained From the Lowering of the Freezing Point
	Observed by De Vries	Observed by Others	
Cane Sugar	1.00	....	1.00
Citric Acid	1.07	....	1.04
NaCl	1.60	....	1.89
KNO_3	1.54	1.76	1.66
K_2SO_4	2.08	2.73	2.11
$MgCl_2$	2.30	2.24	2.64
$CuCl_2$	2.30	....	2.52
Potassium Acetate	1.60	1.66	1.86

It is the same for similar coefficients deduced from the molecular lowering of the vapor tension (boiling point measurements or *tonometry*). Wüllner, in 1858, established the fact that the boiling point of solutions under atmospheric pressure is higher than that of the pure solvent, and the higher the concentration, the greater the rise. Wüllner concluded from his experiments that the lowering of the vapor pressure is proportional to the quantity of the dissolved substance in the same weight of the solvent.

Raoult verified the fact, as in the case of freezing points, that the lowering of the vapor tension depends, in general, only on the ratio of the number of dissolved molecules to the number of molecules of the solvent. With aqueous solutions, that is only true for organic substances. For solutions of inorganic salts in water, we find molecular lowering $\triangle$ deviating from the law for the lowering of the freezing points, and it is shown that

$$i = 5.6m\triangle,$$

$\triangle$ being the diminution of the tension of a one per cent solution of a substance of molecular weight m. We find thus for NaCl, $i = 1.98$, for KNO_3, $i = 1.59$, for K_2SO_4, $i = 1.97$, etc., coefficients agreeing in a satisfactory manner with the values of i obtained from cryoscopic measurements.

Identity of the Coefficients i Deduced from Osmotic, Cryoscopic, and Boiling Point Measurements.—The law of osmotic pressure presents this remarkable peculiarity that not only does it agree with the cryoscopic and boiling point anomalies of salt solutions, but it also permits the determination of the same coefficient *i*, in the three series of phenomena. This has been demonstrated by Van't Hoff,

who supports his proof upon the fact that isotonic solutions have necessarily the same vapor tension, and, inversely, two solutions, having the same freezing point, must have the same osmotic pressure, since they both have as vapor pressure that of ice at the same temperature. It is sufficient to consider cyclic reversible transformations of solutions by means of semipermeable membranes and to apply to them the principles of thermodynamics.*

But, if this reasoning shows that one can obtain the same coefficient *i,* for a definite salt solution, by the three different methods of osmotic pressure, lowering of the freezing point and of the vapor pressure, they do not explain why, for example, a solution of one molecule of sodium chloride in water produces the same effect as about two molecules of cane sugar in the same solvent. It is this gap which the hypothesis of Arrhenius filled, and, at the same time, correlated the electrical conductivity of salt solutions to the coefficients *i,* obtained by the preceding methods.

2. Electrolytic Dissociation of Salt Solutions.

Hypothesis of Arrhenius, Ionization of Electrolytes.†—Arrhenius suggests that the molecules existing in solutions that conduct electricity (aqueous solutions of salts, acids and bases or electrolytes) are not physical molecules such as $CuSO_4$ for copper sulphate, NaCl for sodium chloride, etc., but more simple molecules resulting from the dissociation of these primary ones into different groups, those which Faraday called electric *ions* and into which electricity decomposes the metallic salts, that is to say, SO_4, Cu, Cl, Na, etc. If, then, we take a certain number, N, of molecules of sodium chloride, for example, and dissolve them in water, the total number of molecules present in the solution is not equal to N, but to the number of undissociated molecules plus the number of free molecules. If there are m undissociated molecules and n molecules, each dissociated into $(a+b)$ ions, there will then be $m+n(a+b)$ distinct molecules, and the number of these is necessarily greater than N. Conse-

* J. H. Van't Hoff, *Lois de l'équilibre chimique dans l'état dilué, gazeux ou dissous.*

† Arrhenius presented the different points of this theory in a great many papers published in the *Zeitschrift phys. Chem.* He summarized them in a very complete manner in a memoir published in the French journal, the *Lumière électrique,* of August 31, 1889, and entitled *La théorie moderne de la constitution des solutions électrolytiques,* to which we will refer later.

quently, it is to the number $m+n(a+b)$, of molecules and not to the number N (and it is in this that the hypothesis of Arrhenius consists) that the law of osmotic pressure should be applied. If, for example, all of the molecules of sodium chloride were dissociated into Na and Cl ions, there would be in solution twice as many ions as there were molecules introduced into the solvent, and this would give the equation $PV = 2RT$, which would be absolutely the exact form of the law of osmotic pressures for sodium chloride. As Arrhenius indicated, this is similar to the application of the law of Mariotte to the dissociation of ammonium chloride, at high temperature, into ammonia and hydrochloric acid. If we consider a molecule of NH_4Cl and ascertain the relation between the pressure and the volume of this molecule at a temperature where it is completely dissociated, this relation would not be:

$$P = \frac{RT}{V},$$

where the pressure is expressed as a function of the volume, but

$$P_1 = \frac{2\,RT}{V}.$$

The law of Mariotte applied to this vapor should then be modified into $PV = iRT$, where $i = 2$, for NH_4Cl, exactly the same as the law of osmotic pressures for sodium chloride in aqueous solutions.

Let us assume $\alpha = \frac{n}{m+n}$. Arrhenius calls α the *degree of dissociation* of the solute. The coefficient i, is, from what has just been stated, in the case of ammonium chloride, the ratio of the total number of distinct free molecules, $m+n\ (a+b)$, to the number of molecules introduced, $m+n$, that is, we have,

$$i = \frac{m+n(a+b)}{m+n} = 1+(a+b-1)\alpha.$$

If, then, with Williamson and Clausius, we assume that the electrical conductivity is due to the ions produced from the dissociated molecules, this conductivity should be proportional, according to the theory of Arrhenius, to the coefficient i deduced from the study of osmotic pressures.

From the experiments of Kohlrausch for very dilute solutions of salts, it is evident that the electrical conductivity varies almost proportionally to the amount of the solute dissolved; that is, the conductivity of a column of solution one square centimeter in cross section and one meter long, divided by the quantity of salt dissolved therein, is almost constant when the solution is very dilute. The following table (Arrhenius, *loc. cit.*), shows that this is only true for very high dilutions of KCl, K_2SO_4 and $BaCl_2$:

Concentration Gram Equivalents per Liter	Equivalent Conductivity ($\times 10^{-8}$)		
	KCl	K_2SO_4	$BaCl_2$
1.0	919	672	658
0.1	1047	897	861
0.01	1147	1098	1006
0.001	1193	1197	1092
0.0001	1200	1249	1126
0.00002	1217	1266	1144
0.000011	1216	1275	1142

It is, then, only in an extreme state of dilution (less than one milligram per liter for potassium chloride) that the molecular conductivity may be regarded as constant or, what amounts to the same thing, that the dissociation into ions is to be considered complete. For substances which are poor conductors (mercury salts, acetic acid, etc.), the conductivity never reaches a limit whatever may be the dilution employed.

In cases where a limit of the molecular conductivity may be observed, the degree of dissociation α at a definite concentration will be, by definition, equal to the quotient of the molecular conductivity at this concentration, divided by the limiting or maximum molecular conductivity. For KCl, for example, at the concentration of 0.01, ($\frac{1}{100}$ of an equivalent per liter), we have,

$$\alpha = \frac{1147}{1217} = 0.94.$$

Agreement of the Coefficients Obtained from the Electrical Conductivity and Cryoscopic Measurements.—The coefficient *i*, then can easily be calculated by means of the electrical conductivity* and,

* This calculation is easily made when the maximum molecular conductivity, i.e., the molecular conductivity at infinite dilution, is known. For poor electrolytes this is obtained indirectly by means of a method due to Kohl-

if the hypothesis formulated in order to bring the electrical conductivity, as well as the osmotic pressure, into relation with the proportion of the molecules electrolytically dissociated, and these are exact, one ought to obtain the coefficients i by the electrical conductivity determinations on the one hand, identical with those obtained by the cryoscopic method on the other. This is, indeed, what is shown in the following table of comparison compiled by Arrhenius (*loc. cit.*):

Solute	i observed according to the cryoscopic measurements by Raoult (one per cent solutions)	i calculated from the electrical conductivity
Methyl Alcohol	0.94	1.00
Cane Sugar	1.00	1.00
Barium Hydroxide	2.69	2.67
Potassium Hydroxide	1.91	1.93
Ammonium Hydroxide	1.03	1.01
Hydrochloric Acid	1.98	1.90
Sulphuric Acid	2.06	2.19
Potassium Chloride	1.82	1.86
Sodium Nitrate	1.82	1.82
Potassium Sulphate	2.11	2.33
Barium Chloride	2.63	2.54
Lead Nitrate	2.02	2.08
Copper Acetate	1.68	1.66
Mercuric Chloride	1.11	1.05
Acetic Acid	1.03	1.01

The following are comparisons of values of i obtained by the two methods for potassium sulphate and oxalic acid at different concentrations:

Gram Molecules per Liter	i observed	i calculated	Gram Molecules per Liter	i observed	i calculated
0.036	2.68	2.45	0.069	1.62	1.55
0.091	2.35	2.33	0.131	1.51	1.47
0.227	2.21	2.18	0.247	1.40	1.38
0.455	2.04	2.06			

rausch and Ostwald, based upon the hypothesis that each species of ions has a speed of migration which is characteristic of it. We refer, for the details of this method, which makes use of the observations of Hittorf, to the previously cited memoir of Arrhenius.

The agreement is very satisfactory. Arrhenius himself states "that there are exceptions where the difference is too great to be explained by an error of observation. This occurs especially in the cases of a few weak acids and the sulphates of the heavy metals." Arrhenius, moreover, does not give these contradictory data. We shall, however, have an occasion later to mention a considerable number of them.

Summing up, the hypothesis of Arrhenius leads one to consider aqueous solutions of substances (acids, bases and salts), which yield solutions that conduct electricity as profoundly different from the aqueous solutions of the substances (organic bodies) that yield nonconducting solutions. While the molecules of the solute in nonconducting solutions are simply disseminated and intact in the solution, the dissolved molecules of the electrolytes are more or less dissociated into free ions to which the electrical conductivity of the solution is due. This conductivity is proportional to the degree of electrolytic dissociation. In infinitely dilute aqueous solutions all of the electrolytes are completely dissociated into their ions and give a maximum electrical conductivity. If we consider solutions more or less concentrated, the conductivity decreases in proportion, because the free ions recombine partially and progressively form again the undissociated molecules, and a state of equilibrium is established between the free ions and the undissociated molecules. All of the abnormalities that are presented by salt solutions in comparison to solutions of organic compounds in the most varied experimental lines, osmotic pressure, lowering of freezing points and of vapor pressure, are easily explained by the electrolytic dissociation of the salt in solution, to such an extent that the coefficient *i*, which is a measure of the value of this disagreement, may be deduced by a single experiment in any one of these particular domains.

3. Explanation of Double Decomposition of Salts by the Ionic Theory

This fundamental conception of the constitution of salt solutions was immediately extended to the chemical action involved in the double decomposition of salts by Arrhenius and the advocates of his theory, the foremost among whom is Ostwald. Likewise, in case of electrolytes, this theory postulates that the free ions alone have an active rôle in the transmission of electricity. Also, in the

mutual interaction of salts Arrhenius and Ostwald have endeavored to demonstrate that free ions alone play an active rôle in chemical reactions, by establishing that all reactions at equilibrium involve only dissociations more or less advanced, of physical molecules into ions, and combinations more or less complete of ions among themselves into physically undissociated molecules, whose influence consists only in limiting or favoring the reaction of the ions which they produce. Without free ions or, what is the same thing according to this theory, without electrical conductivity, a solution of an inorganic compound is incapable of reacting upon another solution of an inorganic compound.

We shall pass rapidly in review the principal applications of this electrolytic theory made to the reactions of equilibrium by Arrhenius, Ostwald and Van't Hoff. We shall then present the theoretical and experimental objections which can be made to them.

Additive Chemical Properties.—According to the ionic theory, the chemical properties of salts, acids and bases are none other than those of their ions and are independent of the special properties of the physical molecule. "Silver nitrate, for example," says Arrhenius (*loc. cit.*), "is a reagent for chlorine only when it is present as an ion. When this does not occur, as in potassium chlorate, (whose ions are K and ClO_3), chloracetic acid (H and $CH_2Cl{\cdot}COO$), and several other organic compounds, silver nitrate does not react and it does not form chloride of silver."

The distinctive characteristics of salts in solution, upon which qualitative analysis is almost exclusively based, are then the simple additive properties of their ions, and it is, thanks to the electrolytic theory of dissociation of salt solutions, that one can do without the knowledge of the individual properties of salts in order to distinguish them from each other, on condition of knowing the analytic properties of their ions.

Every element entering into a complex ion loses necessarily its usual reactions and it is the special reactions of that complex ion which alone can be revealed by double decomposition of salts.

Speed of Reactions.—According to the electrolytic theory, the chemical action of an electrolyte ought to depend exclusively on the free ions, for, while an electrolyte produces a chemical reaction in any manner whatever, reversible or irreversible, it is not the total mass of the electrolyte which ought to enter into consideration, in order to promote the reaction, but only the mass of free ions.

The verification of this hypothesis would be very difficult in reactions,—and they are most numerous,—where the electrolyte enters in the reaction, for it would be necessary to study at the same time the speed of reaction and the variation of the electrical conductivity of the electrolyte in order to deduce from them at every instant, the active mass of the free ions. Ostwald referred for the verification of this to a list of chemical reactions where the electrolyte remains unchanged during the transformation. For example, the inversion of cane sugar by mineral or organic acids,

$$C_{12}H_{22}O_{11}+H_2O = 2C_6H_{12}O_6,$$

is a complete irreversible reaction, which takes place at the ordinary temperature in presence of acids whose elements do not enter into the reaction and which remain, consequently, unchanged. If we assume that the activity of the acid, in order to favor this transformation, depends alone upon the mass of free hydrogen ions, it is sufficient then to measure at the beginning the electrical conductivity of the solution of a definite molecular concentration, in order to determine the concentration of hydrogen ions during the reaction.

By comparing the speeds of reaction of different acids, mineral and organic, estimated by the inverse of the time necessary to invert one half of the sugar existing in the solution at the beginning, Ostwald verified, in fact, that these speeds are practically the same for equal concentrations of the hydrogen ions.

Equilibrium Between an Electrolyte and its Ions.—Ostwald, first, and then Van't Hoff, verified the fact that the general law of equilibrium of Guldberg and Waage is applicable to the undissociated molecules and the free ions of an electrolyte.

If we call V the volume in which is dissolved one gram molecule of the electrolyte, μ_v the corresponding conductivity and μ_∞ the conductivity at infinite dilution (complete dissociation), the proportion of the salt dissociated is

$$\alpha = \frac{\mu_v}{\mu_\infty},$$

and the undissociated portion is $1-\alpha$.

If, then, we take a monobasic acid like hydrochloric acid in which the dissociation ions + and — are necessarily equal in number, the concentration of each ion is $\frac{\alpha}{V}$, and that of the undissociated

part is $\frac{1-\alpha}{V}$. The general law of equilibrium $ab = kc$, applied to these masses gives consequently,

$$\frac{\alpha}{V} \times \frac{\alpha}{V} = k\left(\frac{1-\alpha}{V}\right) \text{ or } \alpha^2 = kV(1-\alpha).$$

It is sufficient, then, to measure for different concentrations, the electrical conductivity μ_v of an electrolyte of which μ_∞ is known, in order to ascertain whether the general law of equilibrium is applicable or not.

The accuracy of this hypothesis has thus been verified by two hundred and forty acids, and the results have always agreed in a satisfactory manner with the theory. Here is, for example, the verifications made by Van't Hoff, upon acetic acid at 14°.1 C.

V	100 α	
	Observed	Calculated
0.994	0.402	0.420
2.02	0.614	0.600
15.90	1.66	1.67
1500.00	14.70	15.00
3010.00	20.50	20.20
7480.00	30.10	30.50
15000.00	40.80	40.10

Influence of the Addition to an Electrolyte of an Ion of this Electrolyte.—By the addition of chlorine to the pentachloride of phosphorus which is partially dissociated, the dissociation of the latter is forced back; so Arrhenius* says, similarly, if one considers an acid, like acetic acid, in solution, which contains H and $C_2H_3O_2$, ions besides the molecules $C_2H_4O_2$, and if $C_2H_3O_2$ ions are introduced by adding sodium acetate, which forms ions readily, the quantity of free H ions diminishes and this diminution can be calculated. Let there be a solution containing one gram molecule of acetic acid per liter, let A be the number of $C_2H_3O_2$ ions added without changing the volume and x the degree of dissociation of the acetic acid. The general equilibrium equation gives here:

$$(A+x)x = k(1-x).$$

As x is very small for acetic acid, we can write in an analogous manner:

* *Loc. cit.*

$$Ax = k \text{ or } x = \frac{k}{A}.$$

The quantity of the acid dissociated is then inversely proportional to the quantity A of the free ions of the salts dissolved in the same solution, and the strength of the acid is thus found to be diminished.

Arrhenius verified this conclusion, not by the reaction just mentioned, but by an equilibrium of the same kind; the influence of NH_4Cl upon the saponification of ethyl acetate by ammonium hydroxide, where it is the hydroxyl ions, OH, of the ammonium hydroxide, NH_4OH, which takes part in the reaction

$$C_2H_5 \cdot C_2H_3O_2 + NH_4OH \leftrightarrow C_2H_5OH + C_2H_3O_2 \cdot NH_4.$$

In this case the mass of the OH ions can be estimated by the speed of the reaction of the system:

$$NH_3 + C_2H_5 \cdot C_2H_3O_2 + nNH_4Cl$$

dissolved in 40 liters of water. Here are the results obtained by Arrhenius:

Value of n	Speed of Reaction	
	Observed	Calculated
0.2	22.6	25.2
0.4	12.7	13.0
0.6	9.2	8.8
0.8	7.3	6.7
1.0	6.2	5.4
2.0	3.3	2.8

The agreement is, in fact, very satisfactory.

Mutual Action of Two Electrolytes.—The mechanism of double decomposition of salts is very easily understood from the standpoint of the electrolytic theory. A salt in solution contains the undissociated molecules and its ions in equilibrium. Then, if another salt differing in acid or base be added to the solution, there will be present two undissociated salts and their positive and negative ions. The original equilibrium cannot, in general, subsist; the free positive and negative ions will partially combine, while the undissociated molecules may give new free ions in order to reestablish the equilibrium, and so on, until a new equilibrium is established. At that moment there will be in equilibrium in the

solution, the molecules of the four salts and the four ions resulting from the dissociation of these.

But, if it is easy to understand in terms of the electrolytic theory, the processes of double decomposition of salts, it is more difficult to submit the prediction of the theory to an experimental verification. Arrhenius has succeeded in surmounting this difficulty by the consideration of isohydric solutions, applied first to the mixture of two electrolytes having a common ion, then to the mixture of two electrolytes differing in acid and base.

Isohydric solutions, Arrhenius terms solutions of electrolytes having a common ion and containing the same number of free ions per unit volume. He demonstrates by calculation and verifies by experiment that if the solutions of two electrolytes having a common ion, two acids, for example, HA and HB, can be mixed without producing a change of dissociation, they are isohydric, and inversely. His demonstration will now be given.

Let us call m_a, m_b the number of molecules of each body dissolved respectively in the volume V_a and V_b. Let α_a, α_b, be respectively the degree of electrolytic dissociation of the substances HA and HB. The equilibrium equation applied to the undissociated portion of acid HA and its ions before mixing gives:

$$(1) \qquad k_a \frac{m_a(1-\alpha_a)}{V_a} = \frac{m^2{}_a \ \alpha^2{}_a}{V^2{}_a}$$

when k_a is the equilibrium constant relative to the substance HA.

After mixing, the number of undissociated molecules of HA remains constant as well as that of its dissociated molecules, since, according to the hypothesis, the mixture ought not to modify the degree of dissociation. On the other hand, the number $m_a \alpha_a$, of the H ions has increased by $m_b \alpha_b$ ions, which existed in the solution of HB, and the equation of equilibrium for the acid HA, dissolved now in the volume $V_a + V_b$, is then:

$$(2) \qquad k_a \frac{m_a(1-\alpha_a)}{V_a+V_b} = m_a \alpha_a \frac{(m_a \alpha_a + m_b \alpha_b)}{(V_a+V_b)^2}$$

By multiplying equation (1) by V_a and equation (2) by $V_a + V_b$, the first member of the equations become identical; the second members should be so also, and we have, after removing the common factor, $m_a \alpha_a$

$$(3) \qquad \frac{m_a \alpha_a}{V_a} = \frac{m_a \alpha_a + m_b \alpha_b}{V_a + V_b}$$

We would obtain, likewise, from the equilibrium of the second electrolyte HB:

$$(4) \qquad \frac{m_b \alpha_b}{V_b} = \frac{m_b \alpha_b + m_a \alpha_a}{V_a + V_b}.$$

From which this condition results:

$$(5) \qquad \frac{m_a \alpha_a}{V_a} = \frac{m_b \alpha_b}{V_b}$$

When this condition is fulfilled, the state of dissociation is not then modified by mixing. As $\frac{m_a \alpha_a}{V_a}$ represents the number of ions per unit volume resulting from the dissociation of HA, there is deduced from equation (5) this rule, that the degree of dissociation of two electrolytes having a common ion and containing the same number of ions per unit volume, is not modified when mixed.

In order to verify this conclusion drawn from the foregoing calculation, Arrhenius first employed two solutions of such concentrations that by mixing equal volumes, the conductivity of the mixture would be the mean of the conductivities of the two solutions, in which case the solutions are indeed isohydric. Then he calculated the concentration in hydrogen ions of each and ascertained that these concentrations are in fact practically equal, as is shown by the following table, the calculated concentrations of the H ions for solutions of hydrochloric, oxalic and acetic acid, expressed in milligrams per liter, satisfying the previously given conditions:

Hydrochloric Acid	Oxalic Acid	Acetic Acid
4.48	4.09	3.96
1.33	1.24	1.33
0.379	0.379	0.402

The results are within about five per cent and the agreement is satisfactory.

For the equilibrium in the double decomposition of two salts, AB and A′B′, Arrhenius studied, likewise, isohydric solutions of four electrolytes and ascertained the necessary conditions so that they may be mixed without producing any chemical reaction which corresponds evidently to the equilibrium

$$AB+A_1B_1 \leftrightarrow A_1B+AB_1.$$

By a calculation analogous to the preceding, Arrhenius* finds that volumes *a, b, c, d,* of the four electrolytes in isohydric solution, ought to satisfy the condition

$$ab = cd,$$

in order that the equilibrium may exist after mixing.

In this case, there is not, properly speaking, any possible verification of the conclusions drawn from the theory, all that can be done is to determine *a priori* the coefficient of transformation of double decompositions of salts, and it is sufficient for that to calculate for a mixture of two definite solutions, the volume of the four isohydric solutions of the four electrolytes present, according to the preceding equation. Arrhenius found, for example, for the partition of sodium between hydrochloric and acetic acids, in mixtures of equal volumes of normal solutions, that 99.5 per cent of the sodium combined with the hydrochloric acid and 0.5 per cent with the acetic acid. The quantities of sodium chloride and of sodium acetate thus formed are almost in the same ratio as that of the degrees of electrolytic dissociation of the corresponding acids at the same dilution.

Relative Strength of Acids and Bases.—The relative strength of acids determined by the aid of conditions of equilibrium with respect to the same base are then about proportional to the relative degree of dissociation or ionization. It is the same for bases in respect to the same acid. Speeds of reaction are, likewise, classified according to the order of the degree of dissociation and Ostwald† has thus been led to classify acids and bases into *strong, moderately strong* and *weak* according to their degree of ionization.

The *strong acids* are those that are almost completely ionized and are the halogen hydrides (with the exception of hydrofluoric acid, which is only moderately ionized), nitric, chloric, perchloric, sulphuric, and the polythionic acids. The *moderately strong* acids comprise phosphoric, sulphurous and acetic acids, the dissociation of which is ordinarily between ten and one per cent. The *weak acids* have an ionization of less than one per cent. They are carbonic

* For this calculation see the original paper, *loc. cit.*

†W. Ostwald, *Die Wissenschaftlichen Grundlagen des anal. Chemie,* p. 54. (*Foundations of Analytical Chemistry, translated by Geo. McGowan,* 3d English ed. 1908, p. 57.—*Editors' Note.*)

acid, sulphureted hydrogen, hydrocyanic, silicic and boric acid. The dissociation of the last two is scarcely measurable.

The *strong bases* are, like the strong acids, almost completely ionized. They are the hydroxides of the alkali and alkaline earth metals and the organic quarternary ammonium bases. The *moderately strong bases* are ammonium hydroxide and the amine bases, the hydroxides of silver and magnesium. Finally, the *weak bases,* which are scarcely ionized, comprise the other metallic hydroxides, the amines of the aromatic series (in which the nitrogen is linked to the aromatic nucleus) and the greater number of the alkaloids.

The metallic salts present, in general, much less variation in the degree of ionization than the free acids and bases. The neutral salts of the strong acids and bases are almost completely ionized; those of the moderately strong acids and bases are almost as greatly ionized as the strong acids and bases, for example, ammonium acetate is about seventy-five per cent dissociated. In general, the salts with monovalent ions are almost completely dissociated, and salts with polyvalent ions are less dissociated in proportion as the valency of the ions increases. There are some exceptions to this rule, as for example, the halogen compounds of mercury are very slightly ionized.

Ostwald, likewise, calls attention to the fact that the classification of acids and bases into strong, moderately strong, and weak, has no absolute value. The differences disappear, in fact, when the dilution increases, since ionization increases with the dilution. The law of equilibrium $ab = kc$ gives, in fact, if we call 1 the total mass of the electrolyte, a the part dissociated, and V, the volume of the solution:

$$\frac{a^2}{V^2} = k\,\frac{1-a}{V}, \text{ or } \frac{a^2}{1-a} = kV.$$

an equation which represents the state of ionization of an electrolyte as a function of its dilution V. This equation is that of a hyperbola having for asymptote $a = 1$. Consequently, if V is very large, whatever may be the value of the constant k, the values of a for different acids or bases are practically the same and their respective strengths are equivalent at very high dilutions.

Heat of Neutralization and the Law of Thermoneutrality.—One can calculate with the aid of the electrolytic theory the heat liberated by the chemical reaction between two electrolytes, notably by the

neutralization of acids by bases. Let us consider, for example, a strong acid (HCl), and a strong base (NaOH), and, with Arrhenius assume them to be completely ionized, as well as the product (NaCl) of their reaction. We had before mixing, the free ions, H, Cl, Na and OH, and after reaction, we have as free ions Na and Cl; the only reaction which has been produced is the union of the ions H and OH, to form water, H_2O, dissociated to an infinitely small degree. The heat liberated by this reaction is the heat of combination of the H and OH ions which Arrhenius terms the *heat of dissociation of water.*

Since all the strong acids and bases. as well as the neutral salts which they produce, are practically completely dissociated into their ions, one explains likewise, that the heat of formation of the neutral salts should be obviously the same, whatever the salt, since they are all reduced to nearly the heat of dissociation of the water. Likewise, the mixture of two neutral salts produces no perceptible evolution of heat (Hess' law of Thermoneutrality) because, after the mixing as before, one has only free ions in solution.

One can take into account, moreover, the small fraction of the electrolytes undissociated, as determined by their conductivity, for the exact calculation of their heat of neutralization, as Arrhenius has shown it, and notice that there is an agreement between the heats of neutralization determined by the calorimeter and that deduced from calculation, according to the electrolytic theory.

Another consequence which Ostwald* draws from this theory is the instantaneousness of the double decomposition of salts, that are highly ionized. If a reaction among electrolytes is slow, one may be sure that one of the substances at least is very slightly ionized. This is what takes place notably in phenomena of hydrolysis where water intervenes molecularly in the reaction.

Direction of Transformations by Double Decomposition of Salts.—Starting with these principles, Ostwald assumes that it is in the direction of the formation of the least ionized electrolyte that reactions among electrolytes occur. "Two neutral salts," he says,† "exert almost no action upon one another, because both they themselves and the possible resultant new salts produced by their double decomposition are all strongly ionized and the ions remain substantially in their original condition." . . . "An action takes place, how-

* *Loc. cit.* p. 51.

† *Ibid.* (*3d English Ed.* 1908, *pp.* 64-65.—*Editors' Note.*)

ever, if the ions present are capable of uniting to form one or more compounds, which are either not dissociated at all (practically speaking) or only slightly so under the existing conditions. The constant k has then a small value; in the equation $ab = kc$, a and b (the concentrations of the ions) must therefore become greatly reduced, while c (the concentration of the non-dissociated portion) must grow correspondingly, until the equation is fulfilled."

"The reaction thus results in the more or less complete disappearance of the ions of the electrolyte, which has a small constant, k, going as they do to build up the non-ionized portion."

From this, according to Ostwald, results the neutralization of strong acids by strong bases causing the formation of very slightly dissociated water; the displacement of the weak acid of a salt by a strong acid, because the salt of a weak acid is still considerably dissociated, while the free weak acid is but slightly dissociated; the tendency to the formation of insoluble substances, because the concentration of the ions of insoluble bodies is necessarily very small, etc.

CHAPTER V

OBJECTIONS TO THE ELECTROLYTIC THEORY

The electrolytic theory explains the phenomena of double decomposition of salts with great simplicity, and is certainly very attractive by reason of the advantageous applications which it allows in the varied lines of experimentation, such as osmotic pressures, freezing points, vapor pressures, and electrical conductivities. The extensive studies, which have been occasioned in these later years by the conceptions of Arrhenius, have revealed, as we shall subsequently see, such numerous disagreements between the facts observed and the electrolytic theory, that it seems one can no longer consider the latter but as the expression of an ideal physical law, resting upon too fragile a foundation to base upon it the principles of analytical chemistry.

After having presented as impartially as possible the electrolytic theory of double decomposition of salts, we are now going to discuss it first, from a theoretical point of view, showing that, for a number of incontestable facts, the explanations of our calorimetric theory are equally as satisfactory as those of the electrolytic theory, and that, for the phenomena of hydrolysis, the deductions of the latter are even in contradiction with the direction of the reaction. In the second place, from an experimental point of view, which brings out the fact that, in the very field which Arrhenius has investigated, there are numerous disagreements between the facts and the theory of ionization. We will close this critical examination by indicating how the recent conceptions of the state of polymerization of the solvents and of the solutes can account for the anomalies which necessitate the use of the coefficient i for solutions of salts.

1. Objections of a Theoretical Character

Additive Properties, Speed of Reactions, etc.—We will call attention first to the fact that the additive properties of salt solutions, explained upon the basis of the ionization of electrolytes, can be equally well explained upon the basis of the hydrolysis of salts into free acid and base. It suffices, in fact, to assume the dissociation of

the dissolved substance into any two parts whatever, the acid and base as well as into the ions, each one endowed with specific properties, in order to arrive at the same conclusions.

As to the agreement between the speed of reaction and the conductivity of the electrolytes which produce it, it can depend, in our opinion, upon a much more general cause than the electrolytic dissociation. This agreement is explained, in fact, quite as well, by assuming that the speed of reaction considered by Ostwald,—the inversion of cane sugar by acids,—is expressed by an equation of the same form for all acids. The speed of this reaction which belongs to the category of homogeneous systems with unlimited reaction, ought to obey a law similar to the one applied to the irreversible reactions of the same kind: (Chapter II, § 2),

$$\log\ (1-\frac{y}{p})=-kt$$

in which p is the initial quantity of sugar, y, the quantity transformed in the time t, and k, a function of the temperature, depending upon the strength of the acid employed.

It is, in fact, this law which was verified by the experiments performed in 1850 by Wilhelmy upon the inversion of cane sugar by acids.*

Now, at a constant temperature, and for the same acid, k is a function only of the concentration of the acid, or of a property, a function, itself, of this concentration, such as the degree of hydrolysis, the heat of dilution, the electrolytic dissociation, etc. If, then, we assume $k=f(x)$, x being one of these properties taken as an independent variable, we see that the comparison made by Ostwald between the energy of different acids in the inversion of sugar (see p. 99) is equivalent to comparing the values of t, corresponding to $y=\frac{p}{2}$, that is to say,

$$t=\frac{\log\ (1-\frac{1}{2})}{k}=\frac{A}{f(x)}.$$

A being a constant which has the same value, whatever may be the acid. If the property x, taken as an independent variable, is connected with the concentration of the acid by the same law for all

* W. Ostwald, *Abrégé de Chimie générale,* p. 335, of the French edition.

acids studied, which is not at all impossible, we see then that one ought to find necessarily a perfect agreement between the results of the experiments and those of calculation.

Likewise, it is natural that the study of equilibria between an electrolyte and its ions and between two electrolytes (see page 99). should have given excellent agreement between the experimental and the calculated results, since it is a question here of clearly reversible phenomena, whose state of equilibrium depends exclusively on the concentration of the solute present.

In what concerns the decrease of the activity of an acid by a salt of this acid (addition of an electrolyte having a common ion, page 100) which plays a principal rôle in many important methods of inorganic analysis, it is very simply explained by phenomena of hydration. We shall have occasion, subsequently, to show it in detail in one of the following chapters, apropos of one of these methods (precipitation of metals of the iron group by H_2S in an acetic acid solution). In the example chosen by Arrhenius for his verification (the retarding action of NH_4Cl in the saponification of ethyl acetate by NH_3) the reaction is easily understood, by recalling the fact that NH_4Cl is slightly hydrolyzed into NH_3 and HCl (see page 59). The addition of increasing proportions of NH_4Cl to the ammoniacal system + ethyl acetate, increases the concentration of free HCl proportionally to this addition without changing appreciably that of the free ammonia. And, as we know, from the work of Berthelot and Péan de Saint-Gilles, that the quantity of ester produced in the action of an acid upon an alcohol is proportional to the quantity of acid for a constant quantity of alcohol (see page 70) we see that one can retard the saponification of acetic ester almost proportionally to the quantity of NH_4Cl introduced.

As to the classification of acids and bases, the one Ostwald deduced from their degree of ionization is exactly the same as the one we established from the respective heats of neutralization. The anomalies presented by certain salts are explained just as well by one theory as by the other. We can say, for example, that HgO functions as a strong base and displaces the potassium in its halogen compounds by reason of its heat of neutralization with the halogens, being greater in the case of HgO than with the KOH. The electrolytic theory explains this abnormal displacement by saying that the reaction is produced because there results from it mercury salts which are very slightly ionized.

Finally, the equality of strength of the acids in the state of infinite dilution, deduced by Ostwald from the complete ionization in this state, results in our calorimetric theory, from this fact that in the state of infinite dilution, all salts ought to be entirely hydrolyzed, and their acids set wholly free.

The Law of Thermoneutrality.—Hess' law of thermoneutrality, which has been brought forward as a decisive argument in favor of the electrolytic theory, can equally in our opinion, find an explanation in two very general cases.

1. The first is that every reversible reaction ought to cause some small thermal change. This is confirmed both by theory and experiment. We saw (see Chapter II, § 2) that from the two principles of thermodynamics, there can be deduced that the heat Q liberated by any reaction whatever carried out at the absolute temperature T, is the sum of two terms; one the compensated heat $T(S_A - S_B)$ corresponding to the variation of the entropy S in the initial and final state (a term which may be positive or negative), the other term, the noncompensated heat TP, a term always positive and which represents the fraction of the heat of reaction susceptible of being transformed into mechanical work:

$$Q = T(S_A - S_B) + TP.$$

In reversible reactions (system in equilibrium) the term TP is zero, since any initial modification in a system in equilibrium can produce no noncompensated heat, without which the system would be out of equilibrium and would tend to approach the system giving the term TP = zero. In double decompositions of salts, which are reactions of equilibrium, we have, then,

$$Q = T(S_A - S_B).$$

Now, experiment shows that in reactions, even the most energetic, the compensated heat is reduced to a few hundredths of the total heat liberated, in all cases, where the compensated and noncompensated heat can be estimated separately for example, combustion of carbon monoxide, and reactions employed in electrical batteries.

As the heat of neutralization of acids by the strongest bases does not exceed about fifteen Calories, it is understood that the heat liberated in a double decomposition of salts such as

$$KCl + \tfrac{1}{2}H_2SO_4 = \tfrac{1}{2}K_2SO_4 + HCl,$$

represents only a relatively small fraction of the fifteen Calories; in fact, it is still two Calories or a little more than a tenth of the heat of neutralization of potassium hydroxide by a strong acid (13.7 Cal. with HCl, 15.7 Cal. with $\tfrac{1}{2}H_2SO_4$).

The same conclusions can be verified in the reversible reactions in which ionization certainly plays no rôle. Let us take, for example, the action at high temperature of oxygen on anhydrous metallic chlorides and, inversely, of chlorine on oxides. The reactions are not generally reversible, but, however, there exists a well-known case in which a metallic chloride can be decomposed at will by a current of oxygen and the oxide of the same metal by a current of chlorine. This is the reaction used in the preparation of chlorine by the Weldon-Péchiney process:

$$MgCl_2 + O \leftrightarrow 2Cl + MgO.$$

If the preceding reasoning is correct, the heats of combination of magnesium and chlorine and magnesium and oxygen ought to differ but slightly, so that this reaction liberates but little heat. This is, indeed, what has been found by experiment: Mg+O liberates 143.4 Calories and $Mg+Cl_2$ gives 151.2 Calories. The difference, 7.8 Calories, which represents the heat liberated in the previously mentioned reaction, is even proportionately much greater than the difference between the heats of neutralization of potassium hydroxide by hydrochloric and by sulphuric acids.

We have practically the same thing for the following reaction which is reversible at a high temperature (red heat):

$$Fe_2O_3 + 6H \leftrightarrow 3H_2O + 2Fe.$$

2Fe+3O liberates, in fact, 65.2×3 Calories and 6H+3O, 58.7×3 Calories. The difference scarcely exceeds one tenth of the heat of combustion of iron in oxygen. By taking, one by one, all of the known reversible reactions, one would, likewise, arrive at this conclusion, that in these reactions the heats of combination of the two opposed systems are but slightly different, that is to say, the same law in reality, as that of the thermoneutrality of salts.

2. The second reason for this law can be deduced from a very general empirical law well known in organic chemistry in which it

has been established by numerous examples, namely, that the substitution of one radical for another in respect to bodies endowed with analogous properties, liberates the same quantity of heat.

The inorganic compounds conform to it equally well and innumerable cases can be cited in confirmation of this. Thus, in the substitution of hydrochloric acid for $\frac{1}{2}H_2SO_4$ when in combination with sodium, 2.1 Calories are absorbed, and when in combination with ammonia, 2.05 Calories. That is to say, the same quantity, although the heats of neutralization differ by more than one Calorie:

	HCl	$\frac{1}{2}H_2SO_4$
NaOH dissolved	13.7 Cal.	15.85 Cal.
NH_3 "	12.45 "	14.50 "

This alone suffices to explain the fact that the action of ammonium sulphate upon sodium chloride liberates no heat even if the reaction is complete, because the algebraic sum of the heats of formation of the two opposed systems ought necessarily to be zero. These examples could be easily multiplied by cases of double decomposition of salts, but it seems to us of more interest to show it is the same for reactions among molten anhydrous salts, having very different heats of formation.

Let us take, for example, the chlorides, bromides, chlorates and nitrates of potassium, sodium and ammonium (strong monobasic acids, in combination with analogous metals) and let us calculate from the heats of formation of the salts in the solid state, starting with the elements, what will be the heats liberated by the substitution of Br, (ClO_3) or (NO_3) for chlorine.

Element or Radicals	Heat of Combination of Metals with the Elements in Column I (Anhydrous Salt)			Heat liberated by the substitution of the group in column I for Cl in the Anhydrous Salt		
	K	Na	NH_4	K	Na	NH_4
Cl	105.7	97.9	76.8	....	....	....
Br	99.3	89.8	70.1	— 6.4	— 8.1	— 6.7
ClO_3	93.8	84.8	....	— 11.9	— 13.1	....
NO_3	119.0	110.7	88.6	+ 13.3	+ 12.8	+ 11.8

From this table we see that the substitution of monovalent elements or groups of elements for a monovalent element, when com-

bined with the alkali metals, liberates exactly the same amount of heat; the differences do not reach two per cent of the total heat of combination. So if we consider the mutual actions of any two salts whatever in the preceding table, the heat liberated will be just as small relatively as in the double decomposition of those salts in aqueous solution, although it is a question here of salts whose heats of formation vary within wide limits (from 70.1 Calories to 119).

Ionization, properly speaking, moreover, cannot be assumed, since these facts are absolutely independent of electrical conductivity and are verified in the same manner in the homologous organic series of nonelectrolytes.

Disagreement Between the Phenomena of Hydrolysis and the Deductions of the Electrolytic Theory.—One of the phenomena which contradict most clearly the electrolytic theory is the hydrolysis of salts in aqueous solutions. In the hydrolysis of ferric chloride,

$$Fe_2Cl_6+6H_2O \leftrightarrow Fe_2(OH)_6+6HCl,$$

the electrolytic theory requires the dissociation of water into its hydrogen (H) and hydroxyl (OH) ions, to produce ferric hydroxide and hydrochloric acid. Now, the second system is much richer in free ions than the first, since according to the electrolytic theory, HCl is almost completely ionized, while Fe_2Cl_6 is much less ionized than HCl (in the ratio of about three to five) and water and ferric hydroxide, $Fe_2(OH)_6$, are not ionized at all. It is then, not in the direction of the least ionized system that the reaction tends to be produced, but on the contrary, in the direction of the most ionized system, that is, in the inverse direction to the rule given by Ostwald to predict double decomposition of salts. In fact, the hydrolysis of Fe_2Cl_6 and of most salts, absorbs heat, while the rule formulated by Ostwald has, for its basis, the tendency to form water with the liberation of 13.5 Calories.

In his *Wissenschaftlichen Grundlagen der analytischen Chemie,* Ostwald tries, nevertheless, to connect the phenomena of hydrolysis with electrolytic dissociation. This is the method which he employs.* "Water," says Ostwald, "is a substance very slightly dissociated. However, it contains a certain quantity of free H and OH ions which has been estimated from recent researches at one gram molecule of dissociated ions, in about ten million liters. . . . "

* Pages 64, 65, 3d German Edition (pages 69-70, 3d English Edition.—*Editors' Note*).

"In consequence of this in the process of neutralization of acids and bases, there should remain in reality as many hydrogen and hydroxyl ions as there are normally present in water, this residue being extremely small and negligible in most cases. However, cases may arise in which this small residue of free hydrogen and hydroxyl ions exercises a measurable influence, and these conditions are realized when the acid or base or even both of these are but slightly dissociated, that is, are very weak. The presence of hydrogen ions in the solution of a neutral salt, ought then to give, according to the laws of chemical equilibrium, in combination with the free anions of the salt, a certain quantity of undissociated acid, according to the following equation, $ab = kc$. If k has a large value, as in the case of strong acids, then c is very small, because b (the concentration of the hydrogen ions) is, itself, very small. But, if the value of k is small, then c (the concentration of the undissociated part of the acid) increases correspondingly, and if k approaches in its numerical value to the constant of dissociation of water, then c becomes measurable, and we can recognize in the solution of neutral salt of a similar acid, the presence of this non-ionized acid. Potassium cyanide may be taken as an example of this; hydrocyanic acid has an extremely small constant of ionization, and an aqueous solution of potassium cyanide, therefore, contains a measurable quantity of the undissociated acid, recognizable by its odor."

The explanation of Ostwald is admissible for the salts of extremely weak acids, but it is inapplicable to salts of strong acids like ferric chloride and in a general way to most of the phenomena of hydrolysis.

It is worth while to call attention here to the fact that in many cases the explanations based upon the ionization of salts are exactly the reverse of those that can be deduced from hydrolysis, because the two phenomena are exactly the inverse of each other.

It is, in fact, those salts that are the least decomposed by water into free acid and base (NaCl, K_2SO_4, etc.), that is, with a zero heat of dilution, which are, according to the electrolytic theory, the most strongly ionized, a fact that is shown by a very large molecular electrical conductivity.

Inversely, the most poorly ionized salts, according to the electrolytic theory, i.e., those which yield poorly conducting solutions, are those which are most decomposed in water into free acid and base, that is to say, those whose heat of dilution is large, such as am-

monium borate, ferric chloride, ferric acetate, and, in general, the salts formed from weak acids and bases.

It is, moreover, in conformity with the electrolytic theory that this should be so. Weak acids and bases being much less ionized than the neutral salts which they form, the more a neutral salt of these acids and bases will be decomposed by water into free acid and base, the fewer free ions will it give. *Hydrolysis and ionization are, then, complementary of each other,* for salts of weak acids and bases, and it is for this reason that the tables of classification of acids and bases according to the order of strength, is the same whether one depends upon the heats of neutralization or the degree of ionization.

The uniform result is, then, that one may transpose without difficulty an explanation based on the phenomena of hydrolysis into an explanation founded on the electrolytic theory and inversely, as we shall see subsequently.

2. Objections of an Experimental Character

At the time when Arrhenius proposed his electrolytic theory of dissociation for salt solutions, there had been studied, from the points of view of osmotic pressures, freezing points, boiling points, and electrical conductivity, generally only very dilute aqueous solutions, and the disagreement between the data obtained and the conceptions of Arrhenius were so few that they could be passed over in the presence of the magnificent generalizations allowed by the law of Van't Hoff and the theory of ions, among phenomena so different in appearance.

In fact, the numerous researches inspired by the publications of Arrhenius have all been directed with the aim of confirming his theory. Notably, concentrated solutions or solutions in non-aqueous solvents were left out of consideration for a long time. It is thus that it is admitted, little by little, especially in Germany, thanks to the authority of the illustrious promoters of the electrolytic theory, that aqueous solutions of salts are alone endowed with electrical conductivity, and that the dissolved substances possess abnormal weights, while, in non-aqueous solutions, the solutes have normal molecular weights and, consequently, do not conduct electricity. Ostwald, in his *Grundriss der allgemeinen Chemie,* formulates this rule as follows: "Each time a dissolved substance deviates from the laws of solutions in such a direction that its osmotic pressure (or the change

of freezing point or boiling point, which are proportional to it) is greater than that which corresponds to its molecular weight, this solute is endowed with electrical conductivity, and reciprocally."*

Now, researches, more and more numerous, have shown in these latter years that not only electrical conductivity exists in non-aqueous solutions, but that the molecular conductivity of the electrolytes, which, according to the theory of electrolytic dissociation, should always increase with the dilution, frequently follows an inverse law, even in aqueous solution. We will summarize these researches by examining, first, the non-aqueous solutions of electrolytes, then the aqueous solutions, according to the remarkable memoir published in 1901 by Professor Louis Kahlenberg, of the University of Wisconsin,† who has subjected the electrolytic theory to an extensive series of investigations carried out with scrupulous care, and resulting in the abandonment of this theory.

Non-Aqueous Solutions and Reactions Between Non-Aqueous Solutions Containing Electrolytes.—It has been shown that there exists a large number of solvents other than water, which yield solutions that conduct electricity very well, but which, however, give normal molecular weights and, consequently, indicate that the solute is not at all dissociated. For example, silver nitrate has a normal molecular weight in pyridine and in benzonitrile, and yet these solutions are good conductors of electricity (Werner); the same is true for solutions of the following salts in acetone; cadmium iodide, lithium chloride, sodium iodide, mercuric chloride, ammonium thiocyanate (Dutoit and Friedrich), solutions in urethane of silver nitrate, cadmium chloride and mercuric chloride (Castoro, Kahlenberg) and the solutions in pyridine of succinic, salicylic, and tartaric acids (Jones, Kahlenberg).

A great many salts of metals give in liquid sulphur dioxide solutions that conduct very well, while possessing in this solvent abnormally high molecular weights (Walden); the same is true with liquid ammonia as the solvent (Franklin and Krause).

Numerous anomalies can be cited which are diametrically opposed to the provisions of the electrolytic theory. The electrical

* Edition of 1899, p. 390-391.

† Louis Kahlenberg, *The Theory of Electrolytic Dissociation as Viewed in the light of facts recently ascertained.* (*Bulletin of the University of Wisconsin,* Science Series, No. 4, II, 247 (1901) also *Jour. Phy. Chem.* v, 339 (1901).

conductivity *decreases* with an *increase* of the dilution (NaCl and NaBr in benzonitrile, according to Euler, silver nitrate in pipyridine, according to Lincoln); electrical conductivity increases at first, then decreases with the dilution (Fe_2Cl_6 in paraldehyde, according to Kahlenberg and Lincoln); abnormally low molecular weights in solutions which do not conduct the electric current (solution of diphenylamine in methylcyanide, according to Kahlenberg), etc.

Finally, Kahlenberg has investigated whether, contrary to the electrolytic theory, non-aqueous solutions of salts, which do not conduct electricity, are capable of causing instantaneous double decompositions.* He employed for this purpose a solution of copper oleate in benzene, which does not conduct the electric current and in which, according to cryoscopic measurements, the molecules of copper oleate are undissociated (the freezing point determinations show even that the copper oleate is polymerized). After having verified that a solution of dry hydrochloric acid gas in dry benzene does not conduct any better than the benzene and that the solution attacks neither dry alkaline earth carbonates nor metals (with the exception of zinc), Kahlenberg conducted a current of dry hydrochloric acid gas into a benzene solution of copper oleate, and obtained, in this manner, *instantaneously*, a precipitate of cupric chloride, without the conductivity being modified, at the moment of precipitation. However, the reaction can be represented only by the equation:

$$Cu(C_{18}H_{33}O_2)_2 + 2HCl = CuCl_2 + 2C_{18}H_{34}O_2,$$

a reaction analogous to that of hydrochloric acid upon an aqueous solution of silver nitrate, and yet one cannot maintain that the chlorine and copper ions pre-exist in the solution, since it is a non-conducting solution.

The same results are obtained in these experiments by the substitution of stannic chloride, arsenious chloride, phosphorus chloride or silicon tetrachloride for hydrochloric acid. As in the double decomposition of salts, the solubility of the precipitate is diminished by an excess of the precipitating reagent.

It is established by these experiments that instantaneous chemical reactions can be obtained in perfectly non-ionized solutions, just as well as in solutions belonging to the category of electrolytes.

Experiments of L. Kahlenberg upon Aqueous Salt Solutions.—

*L. Kahlenberg, *Jour. Phy. Chem.*, vi, 1 (1902).

The facts presented above show clearly that the theory of electrolytic dissociation is not applicable to non-aqueous solutions. But the agreements cited by Arrhenius and Ostwald for solutions of inorganic salts in water would still remain strongly confirmatory of the theory, if the experiments undertaken by Kahlenberg upon aqueous solutions had not brought into question a veritable mass of incongruities, more interesting to the domain of analytical chemistry in proportion as the highly concentrated solutions studied by Kahlenberg approach more nearly the usual conditions of analysis than the very dilute solutions almost always employed in support of the theory.

It is fitting then to examine in some detail the experiments of Kahlenberg forming the subject of the before-mentioned memoir of 1901.

In the experiments presented by Arrhenius, the method of comparison of the dissociation obtained from the electrical conductivity and that calculated from the cryoscopic or boiling-point measurements bears within itself a very great cause of uncertainty from this fact that the electrical conductivities have been generally measured at the temperature of the laboratory while the cryoscopic measurements have been made below zero degrees and boiling-point determinations above 100°.

To escape from this source of error or at least make it negligible, Kahlenberg measured the electrical conductivities at zero degree, in order to compare them with the data of the freezing-point determinations, and near 100° to compare them with the boiling-point measurements. Under these conditions, the molecular weights deduced from the freezing-point or boiling-point measurements may be rationally compared to the electrical conductivity obtained at corresponding temperatures.

The experiments, carried on with all of the necessary precautions to eliminate the causes of errors due to the impurities of the reagents or the variation of temperature, have dealt with a large number of common typical salts in solutions varying in concentration from very dilute up to very strong (1 to 4 equivalents per liter).

The following table indicates the salts used in each class of measurements.*

* The electrical conductivity cannot be measured exactly at 100°, because the bubbles of vapor which are formed at this temperature upon the electrodes modify the resistance and introduce errors. This is why the measurements have been made only at 95°. For cryoscopic determinations a large number

	Chlorides	Bromides & Iodides	Nitrates	Chlorates	Sulphates
Conductivity at 0° (19 salts)	Na, K, Ba	KI	Na, K, Ba Sr, Ag	K	K, Mg, Mn Zn, Fe, Ni Co, Cd, Cu
Conductivity at 95° (18 salts)	Na, K, Mg Ba, Hg	KBr KI	K, Aσ	K	Mg, Zn, Mn Fe, Ni, Co Cd, Cu
Cryoscopic Measurements (9 salts)	Na	....	....	....	Mg, Zn, Mn Fe, Co, Ni Cd, Cu
Boiling Point Measurements (18 salts)	Na, K, Mg Ba, Hg	KI KBr	K, Ag	K	Mg, Zn, Mn Fe, Ni, Co Cd, Cu

In general the results obtained are grouped around a small number of types and it is sufficient to mention a few of them in order to understand them all.

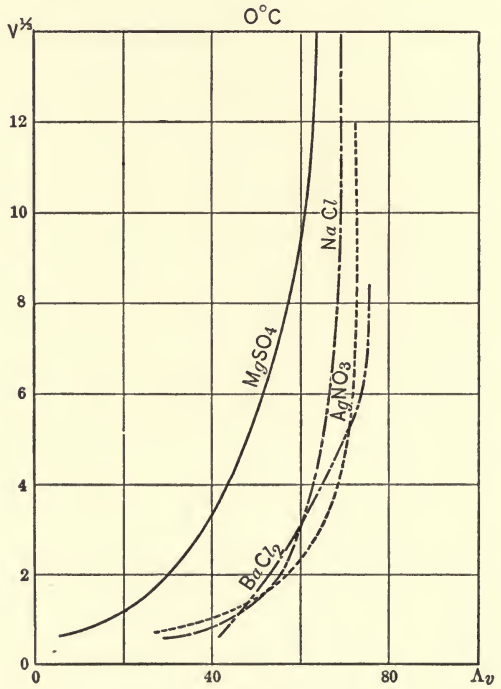

Fig. III

Electrical Conductivity at 0°

of measurements have been made by other experimenters, consequently he was able tc reduce the number of salts with which it was necessary to work.

1. *Electrical Conductivity.*—The accompanying curves taken from Kahlenberg's memoir, represent by the abscissas the equivalent conductivity Λv; by the ordinates, the cube root of the corresponding volume in liters, containing one gram-equivalent; and allow a ready comparison of the phenomena for four salts taken as types: NaCl, $BaCl_2$, $AgNO_3$ and $MgSO_4$.

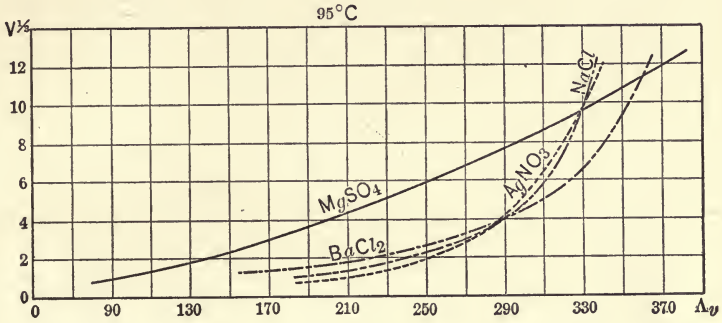

FIG. IV

Electrical Conductivity at 95°C

The curves representing the chlorides and nitrates are the same; the sulphates give a flatter curve, particularly at 95°, when it becomes almost a straight line; potassium chloride and potassium iodide give curves almost identically the same as that for sodium chloride.

There is no disagreement in this in comparison with the theory of Arrhenius; in general, the molecular conductivity increases regularly with the dilution and reaches a well-defined limit, especially at 0°.

2. *Cryoscopic Measurements.*—The salts can be grouped into three classes according to the results obtained: Salts whose molecular weights do not vary perceptibly with the concentration (type NaCl); those whose molecular weights increase regularly with the concentration (type $MgSO_4$, to which belongs $FeSO_4$): finally, those whose molecular weights show a very marked maximum for a definite concentration (type $MnSO_4$, to which belong the sulphates of Zn, Co, Ni, Cd and Cu). Below are given the data obtained for each of these three types:

Sodium Chloride: NaCl. Mol. Wt. 58.5

Weight of Anhydrous Salt in 100 g Water	Lowering of the Freezing-Point	Corresponding Molecular Weight
1.195	0.693	32.6
2.550	1.512	31.9
2.970	1.750	32.1
3.927	2.300	32.3
4.914	2.866	32.4
5.741	3.395	31.7

Magnesium Sulphate: $MgSO_4$. Mol. Wt. 120.4

Weight of Anhydrous Salt in 100 g Water	Lowering of the Freezing-Point	Corresponding Molecular Weight
0.699	0.154	85.8
1.517	0.314	91.3
2.550	0.480	100.4
5.994	1.006	112.6
6.961	1.165	112.9
9.246	1.527	114.5

Manganese Sulphate: $MnSO_4$. Mol. Wt. 151.1

Weight of Anhydrous Salt in 100 g Water	Lowering of the Freezing-Point	Corresponding Molecular Weight
1.941	0.293	125.2
2.502	0.361	131.0
5.120	0.687	140.9
10.843	1.399	146.5
18.572	2.591	135.5

For sodium chloride we see that, between the limits of concentration studied (about 0.2 to 1.0 normal) the molecular weight remains practically constant: it is 32.6 for 0.2 normal which corresponds to a dissociation of 79.4 per cent, and of 31.7 for the almost normal solution, which corresponds to a dissociation of 84.0 per cent. From the observed electrical conductivity, the degree of dissociation calculated from the usual formula $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$, is 79 per cent for the 0.2 normal solution and 70 per cent for the normal solution, the values corresponding respectively to the molecular weights 32.7 and 34.4. There is then almost complete agreement between the molecular weights obtained by the two methods (conductivity and cryoscopy),

conforming with the theory of Arrhenius, but it is to be noted that, while the electrical conductivity increases with the dilution the freezing points seem to indicate a constant and even decreasing dissociation with an increase in the dilution.

For magnesium sulphate (whose concentrations studied have varied between 0.1 and 1.5 normal) dissociation has varied correspondingly between 40 per cent and 5 per cent by the freezing-point method, while the electrical conductivity gives a dissociation varying between 44 and 22 per cent respectively. There is then little difference between the two methods for dilutions of 0.1 normal; but the disagreement becomes greater with an increase in the concentration.

Finally, for manganese sulphate, there is complete disagreement; while the electrical conductivity increases regularly with the dilution, showing by this method an increasing dissociation and a decreasing molecular weight, cryoscopic measurements show very clearly a maximum molecular weight 146.5, corresponding to a dissociation of 3 per cent, while by the electrical conductivity for the same dilution we have a dissociation of 20 per cent.

For the other sulphates of the same type the following maximum molecular weights were obtained by the cryoscopic measurements as well as the corresponding concentrations:

	Normal Molecular Weight	Maximum Molecular Weight	Concentration Per Cent
$ZnSO_4$	161.5	173.1	13.675
$CdSO_4$	208.1	223.6	15.640
$CoSO_4$	155.1	171.2	9.657
$FeSO_4$	152.1	158.4	8.980
$CuSO_4$	159.7	175.4	9.243

For all of these concentrations, in the vicinity of 10 per cent, when the salts are certainly not dissociated according to the cryoscopic measurements, the electrical conductivity shows dissociations of about 25 per cent: the difference is then very marked.

These disagreements for the sulphates of the magnesium series, which are perceptible even in low concentrations, had not escaped Arrhenius, who had explained them by assuming that non-dissociated molecules are polymerized in aqueous solution, which counterbalances the effect of ionization of the dissociated molecules according to the cryoscopic measurements; this hypothesis he supports upon the marked variation of the speeds of migration in the electrolysis of $MgSO_4$ and $ZnSO_4$, depending upon the concentration. What diminishes, however, the value of this explanation is that Hittorf

has verified the same thing for other salts where the agreement between the electrical conductivity and cryoscopic measurements is satisfactory (notably for chlorides and nitrate of the alkaline earths and magnesium chloride). Anomalies of the same kind have been noticed by other experimenters in their cryoscopic and boiling-point measurements: *minimum* lowerings of the molecular weights for $MgCl_2$ and $BaCl_2$ between certain limits of concentration (Jones and Chambers), variations of molecular weight with the dilution of phosphoric acid, sulphuric acid, etc., in the inverse to that anticipated according to the electrolytic theory (Dieterici), etc.

3. *Boiling-Point Measurements.*—The salts studied can be grouped under three classes: Salts whose molecular weights decrease when the concentration increases (chlorides of the alkalies and alkaline earths, potassium bromide and iodide); those whose molecular weights increase with the concentration ($HgCl_2$, $KClO_3$, alkali nitrates); finally, salts whose molecular weights reach a maximum (all of the sulphates studied).

Below is given an example of each type:

Sodium Chloride: NaCl. Mol. Wt. 58.5

Weight of Anhydrous Salt in 100 g Water	Rise of the Boiling-Point	Corresponding Molecular Weight
1.139	0.197	33.4
4.167	0.744	32.4
5.524	1.002	31.9
8.254	1.553	30.0
11.010	2.157	29.5
15.910	3.304	27.8
20.520	4.495	26.4

Potassium Chlorate: $KClO_3$. Mol. Wt. 122.6

Weight of Anhydrous Salt in 100 g Water	Rise of the Boiling-Point	Corresponding Molecular Weight
3.743	0.34	57.2
8.121	0.65	66.4
12.837	1.01	66.0
17.116	1.31	67.9
23.484	1.72	70.9
29.689	2.10	76.7
35.42	2.49	73.9
42.96	2.98	74.9
48.92	3.43	74.1

MAGNESIUM SULPHATE: $MgSO_4$. MOL. WT. 120.4

WEIGHT OF ANHYDROUS SALT IN 100 G WATER	RISE OF THE BOILING-POINT	CORRESPONDING MOLECULAR WEIGHT
2.733	0.097	146.5
7.236	0.281	168.6
27.58	0.524	273.7
36.91	0.925	207.5
43.47	1.455	155.4
52.77	1.984	138.3
60.52	3.220	97.7
64.39	3.316	101.0
72.28	3.630	105.9

For the first class (molecular weight decreasing with the increase of concentration) there is an *absolute opposition* to the ionic theory, to such an extent that, for sodium chloride, it would be necessary to assume that, above 20 per cent, the molecule is dissociated into more than two ions, since the molecular weight is less than half of the normal molecular weight, and yet the equivalent electrical conductivity decreases regularly with the concentration up to 20 per cent. For KCl, KBr and KI, the molecular weight also becomes finally less than half of the normal molecular weight and for $MgCl_2$ and $BaCl_2$, less than one third.

The second class (molecular weight increasing with the concentration) is the only one which agrees with the electrolytic theory. The agreement, which is very satisfactory for the nitrates of potassium and of silver, is much less so for potassium chlorate (for the concentration giving a molecular weight of 66, the dissociation is 86 per cent by the boiling-point method and only 70 per cent by the electrical conductivity).

For the third class (with maximum molecular weights), the results are, as for the cryoscopic determinations of the sulphates, in complete disagreement with the results of the electrical conductivity, which increases regularly with the dilution. If we compare the data in the tables of cryoscopic and boiling-point measurements, we are impressed with the fact that, with equal concentrations, *the boiling-point determinations give much larger molecular weights than the cryoscopic measurements.*

If we assume that the molecules are polymerized it follows that that polymerization is greater at the boiling-points than at the freez-

ing-points—this appears very improbable. Kahlenberg has very justly called attention to this fact.

The well justified conclusion that Kahlenberg draws from these numerous experiments is, that, "the difficulties which the theory of electrolytic dissociation encounters in explaining the phenomena in aqueous solutions are really insurmountable."

Transfer of Dissolved Electrolytes, Experiments of Chassy.—It remains for us finally to say a few words about the studies of the transfer of electrolytes made in 1890 by M. Chassy in the laboratories of the Sorbonne, which, although undertaken in the domain of electrolysis, that is to say, the one more favorable to that theory, appear equally to cause the rejection of the theory of electrically charged ions *pre-existing in the free state* in aqueous salt solutions.

We know that, when a salt solution is subjected to electrolysis there are produced two phenomena, distinct in appearance. On the one hand, the ions of the electrolyte are set free upon the electrodes, and upon the other hand, the concentration of the electrolyte in different parts of the solution is modified. It seems as though there had been a *transfer* of the undecomposed salt molecules toward one of the two electrodes.

Hittorf, who first studied, in 1853, these phenomena of migration, in an exact manner, explained them by assuming that the free ions alone move in the electrolyte, the positive ions toward the negative electrode, the negative ions toward the positive electrode, this course being made with *different speeds of migration* according to the ions. It is the residues of the ions that have not had time to reach the electrodes, which, in this theory, reform the physical molecules, differently distributed in the electrolytic bath from what they were at the beginning.*

Hittorf's hypothesis, adopted by the advocates of the electrolytic theory of salt solutions, is then in fact based upon the pre-existence of free ions in these solutions.

Now the researches carried on by M. Chassy upon the transfer of electrolytes, not only with a single salt in solution, but with mixtures of several salts, lead to very different results. From a recon-

* This redistribution permits the deduction of the relative speeds of migration of which Ostwald has taken advantage to determine the relative electrical conductivity, for a given concentration, of an electrolyte whose limit of conductivity for an infinitely dilute solution cannot be determined directly.

sideration of the data of the experiments of Chassy, Ponsot has in fact, deduced the following two laws:*

1. "In the electrolysis of a mixture of salts of the same acid of which one is electrolyzed, the total number of transferred molécules depends only upon the nature and the concentration of the electrolyte. It is independent of the pressure of non-electrolyzed salts and of their concentration."

2. "When there are two electrolyzed salts, the total number of molecules transferred depends upon the nature of the salts, their concentration and the fraction of an equivalent of each of them electrolyzed. It does not depend upon the non-electrolyzed salt and acid added to the two preceding."

These results do not seem compatible with the theory of ions, as Ponsot has justly indicated. The experiments of Chassy show in fact that, in a mixture of several salts, one alone can be electrolyzed (which is shown by the metal deposited upon the negative electrode) and the transfer of molecules by the electric current can be shown at the same time although they have not been dissociated into ions. One can even deduce from the first law that the transfer of the molecules only of the electrolyzed salt is accomplished in the *physical state without previous ionization*. The law being true, in fact, even if the number of salts in solution is reduced to one, it is natural to assume by reason of continuity that the transfer of the molecules of this one salt is accomplished in the same way as the transport of the molecules of the non-electrolyzed salt, that is, without having undergone electrolytic dissociation, which is absolutely contrary to Hittorf's hypothesis,—which is, itself, one of the fundamental conditions of the theory of ions.

3. The Polymerization of Solvents and of Solutes

If the contradictions between the facts and the theory of ionization appear to require the rejection of the latter, one falls then into another difficulty, that of not explaining the necessity of introducing the coefficient i into the general law of equilibrium of Guldberg and Waage. Without doubt it would be better to renounce this explanation rather than to derive it from a contestable hypothesis. Recent researches, however, upon the state of polymerization of liquids undertaken by Ramsay and Shields, and the applications which

* *Comptes Rendus*, cxxxviii, 192 (1904).

Professor H. Crompton has made of polymerization to salt solutions, allow henceforth the conception of the coefficient i as resulting from a chemical action between the solvent and the solute. These researches throw a new light upon the disagreements that are presented by salt solutions, in comparison with one another, and permit, particularly, a much better comprehension of the anomalies pointed out in the experiments of Kahlenberg. It appears then necessary to us to indicate these principles and to summarize briefly its consequences.

Experiments of Ramsay and Shields.—By endeavoring to measure the molecular mass of bodies in the liquid state Ramsay and Shields have been led to formulate, in 1894, a law which is not without analogy with the law of osmotic pressure.*

The method employed by these workers to measure the molecular weights of liquids is based upon the relation which exists between the molecular mass and the surface tension of the liquid causing the phenomena of capillarity. If we consider two liquids in contact, the surface energy is manifested by the fact that it is necessary to expend a certain amount of work σ to increase the separating surface of the two liquids by a quantity Δs, and experiment shows that the ratio

$$\frac{\sigma}{\Delta s} = \Upsilon$$

is a constant, at a given temperature, for two definite liquids.

This coefficient Υ is what is ordinarily called the *surface tension* of the two liquids. Its value for a liquid and its vapor, for example, is easily determined by means of a special apparatus devised by Ramsay and Shields, by measuring the height to which the liquid rises in a capillary tube containing the vapor of the liquid and by employing the known formula

$$\Upsilon = \tfrac{1}{2}\, g\, r\, h\, (\rho - \delta)$$

in which g is the acceleration of gravity, r is the radius of the capillary tube, h is the height the liquid ascends in the capillary tube, ρ and δ are the densities of the liquid and vapor, respectively, at the temperature of the experiment.

The experiments show that, in the case of a liquid and its own vapor, γ decreases with an increase in the temperature, becoming zero at the critical point; and it is the same with the *surface energy*

*W. Ramsay, *l'Energie de surface pour déterminer la complexité moléculaire des liquides* (Lectures before *la Société Chimique de Paris*, 1893 to 1900, p. 27).

γs (produced from γ by the surface s separating the liquid and its vapor), if we take s constant. If then we express as ordinates the temperature and as abscissas the value of the surface energy, we will obtain, for a given liquid a curve expressing this energy as a function of the temperature.

The experiment shows that, for all liquids whose critical point has been determined, the curve has the form as represented in Figure V.

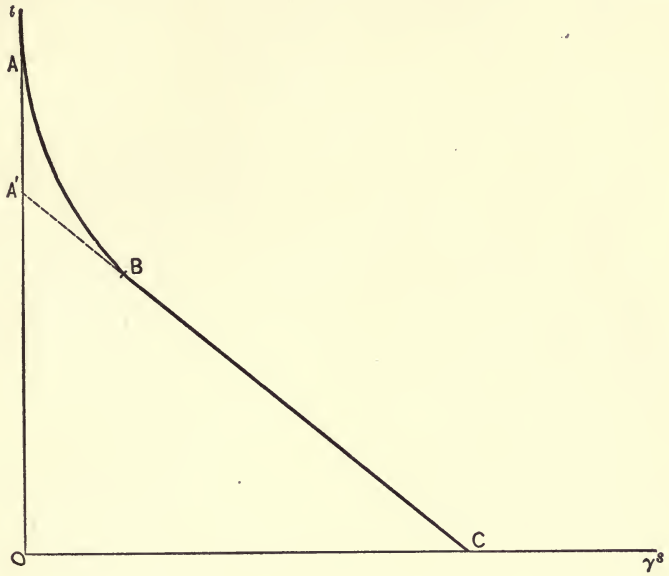

FIG. V

From A (critical point where $\gamma s = 0$) to B (at a few degrees below the critical point) it presents a curvilinear form; then it takes the form of a straight line BC. Leaving out of consideration the curved portion, the surface energy is represented for certain temperatures below the critical temperature, by the linear equation:

$$\gamma s = k\,(t - \theta) \tag{1}$$

in which k is a constant, t the variable temperature counted from the critical temperature down, and θ a constant equal to AA'.

We can express comparison between two liquids: For that purpose, we can, just as is done for gases, consider *equimolecular surfaces* of these liquids, that is, plane surfaces containing the same

number of assumed molecules distributed at an equal distance from one another, and compare the equations (1) relative to each of these liquids, in which s is an equimolecular surface. If we designate, by v, the volume of the unit mass of a liquid, by M the mass of its molecular weight, the product Mv represents for all the liquids, volumes containing the same number of molecules, assuming that the molecules are *simple* and not *polymerized.*

The two-thirds power of the products Mv will then represent equimolecular surfaces for each of these liquids and equation (1) becomes:

$$\gamma(Mv)^{\frac{2}{3}} = k(t - \theta), \tag{2}$$

an equation analogous to that of the perfect gases

$$p(Mv) = k(t - \tau),$$

where p represents the pressure and τ an interval of temperature analogous to the interval θ.

Ramsay and Shields, by comparing the established equation (2) for a certain number of liquids at their known critical temperatures, have ascertained that k *is a constant* whose average value is 2.12. The following are, in fact, the values of k for a few organic liquids:

Liquid	k
Ethyl Ether	2.1716
Methyl Formate	2.0419
Ethyl Acetate	2.2256
Carbon Tetrachloride	2.1052
Benzene	2.1043
Chlorbenzene	2.0770

In most cases the critical temperature is not known, but the value of k can then be determined by measuring the surface tension at two different temperatures, which permits the elimination of θ between the two corresponding equations (2) and results in the relation

$$k = \frac{\gamma(Mv)^{\frac{2}{3}} - \gamma^1(Mv^1)^{\frac{2}{3}}}{t - t'} \tag{3}$$

in which all of the terms are known, $t - t'$ being equal to the interval of temperature of the two experiments. This relation is exactly the same as that given by the Mariotte-Gay Lussac law for perfect gases:

$$R = \frac{pMv - p'Mv'}{t - t'}.$$

If, then, for a given liquid, it is found that k differs notably from the average value, 2.12, it is because just as for dissociated gases, the hypothesis from which we started (the invariability of the number of the molecules in the molecular weight, whatever may be the liquid) was not legitimate. We must conclude from it that M was badly chosen and that it is necessary to multiply it by a coefficient x in such a manner that the equation

$$\gamma(xMv)^{\frac{2}{3}} = 2.12\ (t - \theta) \qquad (5)$$

be verified, absolutely, as in the case of dissociated gases (ammonium chloride, iodine vapor, sulphur vapor, etc). It is necessary to multiply M by a certain factor in equation (4) in order to obtain the constant R. In these cases, the coefficient x may be considered as being the number of simple molecules which are associated to form a complex liquid molecule. It is easily calculated by means of the equation (5).

Ramsay and Shields have thus found by determining γ at different temperatures, that x varies for alcohol from 1.64 at 20° to 1.06 at 210°, for water from 1.71 at 0° to 1.29 at 140°, etc. As the value of k is a little uncertain, x is determined only within about 15 per cent for water. For example, if, however, the degree of association is not known with a great accuracy, the principle itself of this association, or *polymerization,* is placed beyond a doubt by the method of Ramsay and Shields. Their experiments, made upon a great number of liquids, have shown that most bodies possess in the liquid state the same molecular size as in the gaseous state, but, in general, compounds containing the OH group are an exception to this rule, particularly, water, alcohol, acetic acid, etc. So that water, for example, should be considered as containing in the state of equilibrium simple and condensed molecules, the equilibrium depending upon the absolute temperature, just as for the vapors of sulphur and iodine.

H. Crompton's Theories of Coefficient i.—The analogy of the conclusions of Ramsay and Shields with those of Van't Hoff, resulting in the equation $PV = iRT$ of the law of osmotic pressure, for salt solution is striking. The coefficient x plays in the equation

of Ramsay and Shields the same rôle as the coefficient *i* in Van't Hoff's equation.

Guided by the analogy, Professor Holland Crompton introduced this new notion of the polymerization of liquids, which he extended equally to dissolved bodies, into the demonstrations given by Arrhenius and Van't Hoff upon the laws of osmotic pressure and of the lowering of the freezing points. He has been able thus to demonstrate in an exact manner that the anomalies of the aqueous solutions of metallic salts in comparison to organic solutions spring necessarily from the relation which exists between the state of aggregation of the solvent and that of the dissolved substance, which varies with the concentration. It is sufficient to assume that this tends towards the non-molecular state in infinite dilutions in order to explain and obtain the coefficient *i* just as easily as with the hypothesis of electrolytic dissociation.*

The *quasi*-constancy of the heat of neutralization of the acids AH by the bases BOH comes according to Crompton's theory from the immediate polymerization of the water HOH, resulting from this neutralization, and the absence of the evolution of heat in reactions among salts (thermoneutrality) depends upon the fact, in this case, that there is no formation of water, and consequently no modification in the state of association of the solvent.

Reychler's Hypothesis.—Along the same theoretical lines, the chemist Reychler† starting from the principle that hydrolysis is the fundamental phenomenon accompanying the solution of metallic salts in water, assumes that a salt MA gives a reversible reaction either with the simple molecules of water, or with its associated molecules:

$$M{\cdot}A + H{\cdot}OH \leftrightarrow M{\cdot}OH + H{\cdot}A,$$

$$M{\cdot}A + \frac{1}{n}(H{\cdot}OH)n \leftrightarrow M{\cdot}OH + H{\cdot}A,$$

and this would be the continuous displacement of the constituent parts of salt in ephemeral combination with the H·OH of the solvent, or *mobile ions,* which would explain, according to him, the formation of electric currents, the law of thermoneutrality, the *quasi*-constancy of the heats of neutralization and the sharpness of analytical reactions.

* For these demonstrations see the original articles of Holland Crompton, *Jour. Chem. Soc.,* lxxi, 925, 946 and 951 (1897).

† Reychler, *Journal de chimie physique,* ii, 307 (1904) Genève.

Without following this author so far as the electrical consequences which he believes it is his duty to deduce from the hypothesis of mobile ions, we assume with him that the phenomena of hydrolysis suffice to explain the mechanism of reactions between aqueous salt solutions, and that the two parts into which a salt dissolved in water ought necessarily to separate in order to produce a double decomposition are not hypothetical electrical ions, but a *real* base and acid coming from the chemical action of water upon the salt in solution.

Conclusion.—The great number of facts in contradiction to the electrolytic theory leads us then to renounce the hypothesis of ions and its consequences in explaining the constitution of salt solutions and the double chemical decompositions which they cause.

The electrical conductivity of electrolytes ought to be classified provisionally in the category of specific properties analogous to the electrical conductivity of the solid bodies which we observe among metals and which does not exist in other substances, without our being able to explain the difference.

It does not follow that everything is to be rejected in the Arrhenius-Ostwald theories, for it seems indeed that there is in this conception a sort of reflection of a limiting-law analogous to that of perfect gases. But as Kahlenberg* points out, while this limiting-law of perfect gases might have been extended by Van der Waals in an uninterrupted manner to gases more and more condensed, by means of coefficients which, decreasing little by little, finally terminate in the theoretical law, it is not the same in the case of the electrolytic theory, whose conceptions, perhaps valuable for infinite dilutions, show formal contradictions when one tries to apply them to solutions more and more concentrated.

These contradictions depend upon the fact that the formulation of Arrhenius includes phenomena too dissimilar and leaves out of consideration an important phenomenon: the chemical action of the solvent upon the dissolved substance, which action plays precisely so important a rôle in hydrolysis,—the very phenomena in which is manifested most clearly the inadequacy of the electrolytic theory. A salt which is dissolved in water diffuses throughout the same in a manner similar to that of a gas in a vacuum, but only upon the condition that we leave out of consideration the liquid; for, in reality, the salt does not diffuse into the liquid by virtue of its elastic

* *Loc. cit.*

strength as a gas, but by reason of a special affinity which is indicated by osmotic, cryoscopic phenomena, etc. This affinity connected with the state of aggregation of the molecules of the solvent and of the dissolved substance suffices to explain, as we have just seen, the anomalies of salt solutions in comparison to solutions of substances not salts. The difference between the phenomenon of expansion of gases and that of solubility is again shown by this fact that while all gases mix (in all proportions) solids do not dissolve in the same way in all liquids (Kahlenberg).

We are going to depend, in studying methods of analytical chemistry based upon double decompositions of salts, exclusively upon principles deduced from our calorimetric theory to which the new conceptions of the polymerization of solvents and solutes are not only not contradictory, but rather add a greater strength by clearing up the general law of equilibrium.

CHAPTER VI

GENERAL PROCESSES OF ANALYSIS BASED UPON DOUBLE DECOMPOSITIONS OF SALTS

1. Methods of Producing as Complete Precipitation as Possible

Influence of an Excess of the Reagent.—Until the middle of the nineteenth century, chemists, in view of the production of insoluble precipitates, assumed implicitly that the reaction is effected in a complete manner in conformity to the equation of reaction, and their dominating thought was to place themselves within the exact conditions of the equation. That is to say, to introduce into the liquid the equivalent of the reagent exactly necessary to make the double decomposition with the salt containing the constituent to be precipitated. This is what results, for example, in conditions recommended by Rivot for the precipitation of barium sulphate with the object of determining the sulphuric acid in a sulphate: "By avoiding an excess of the reagent," he says,* "we have the advantage of obtaining barium sulphate almost pure and very easy to wash." It is very true that the manipulation indicated by Rivot necessarily implies the addition of a slight excess of the reagent: "We dilute with considerable water, add a little hydrochloric acid and pour in a solution of barium chloride until a precipitate begins to form." What the author seeks especially in this case, is evidently to limit as much as possible the carrying down of the barium chloride by the sulphate which, as we know, retains the chloride firmly.

In the case of other reactions, nevertheless, we see appear Rivot's ideas of adding an excess of the reagent when the precipitate is considered somewhat soluble in the mother liquor. This is true for the precipitation of phosphoric acid in the form of magnesium ammonium phosphate. Rivot indicates that the precipitation is more complete when one employs an excess of the reagent. To keep, however, the precipitate from retaining a considerable quantity of magnesium sulphate in spite of the washings, he recommends the use of only a small excess, without moreover otherwise indicating the proportion.

* Rivot, *Docimasie*, 2d edition, I. 234.

The work of H. Rose, of Mulder, of Fresenius, of A. Carnot, etc., in establishing the best conditions of insolubility of a large number of precipitates employed in analytical chemistry, have shown that, in most cases, the insolubility of the precipitate is increased by the addition of a greater or smaller excess of the precipitating reagent: of lead sulphate, by the addition of a slight excess of sulphuric acid (H. Rose); of ammonium phosphomolybdate, by a large excess of a nitric acid solution of molybdic acid (Sonnenschein); of silver chloride, by a small excess of silver nitrate, if it is a question of the precipitation of chlorine; or by the excess of sodium chloride, if one desires to determine the silver (Mulder), etc.

It is the early work of Mulder upon the determination of silver* which appears first to have clearly shown the rôle of an excess of the reagent. Silver chloride is completely insoluble in pure water or in water slightly acidified with nitric acid. However, on investigating whether one equivalent of sodium chloride dissolved in water precipitates exactly and completely one equivalent of silver dissolved in nitric acid, we find that this does not happen. The clear supernatant liquid in contact with the precipitate, gives a cloudiness when a little of the solution of sodium chloride is added as well as when silver nitrate solution is introduced. As Mulder has demonstrated perfectly, if into a silver solution, for example, a standard sodium chloride solution has been introduced until there is no longer formed any precipitate of silver chloride, an excess, necessarily, of sodium chloride has been added beyond the quantity required by the equation

$$AgNO_3 + NaCl = AgCl + NaNO_3,$$

and it is only due to this excess of sodium chloride that all of the silver has been precipitated.

A hundredth normal solution of silver then added to the clear filtrate gives a precipitate of silver chloride, and Mulder showed that it was necessary to add one cubic centimeter of the hundredth normal silver solution to have no further precipitate. If to this new liquid, which contains silver nitrate in excess, we add a hundredth

*G. J. Mulder, *Scheikundige Verhandelingen en Onderzoeking*, 1857. Fresenius (p. 255 of the 6th French edition) has presented a résumé of the observations of Mulder: (see Cohn's translation of the 6th German edition of Fresenius, Vol. I, p. 344-345.—*Editors' Note*).

normal solution of sodium chloride there is required exactly one cubic centimeter of this $\frac{N}{100}$ solution in order to no longer have a precipitate of silver chloride.

If we were to add only one half a cubic centimeter we would have what Mulder calls the *point of neutrality;* i.e., the point for which it is necessary to have the same quantities of a hundredth normal solution of silver nitrate and of sodium chloride, to no longer have any precipitate of silver chloride, that is, 0.5 c.c. of either liquid. Since one cubic centimeter of a hundredth normal solution corresponds to one milligram of silver, it is seen that according as one titrates the standard silver solution with sodium chloride or one titrates in the reverse order with a hundredth normal silver solution, results are obtained which differ by one milligram of silver or one-thousandth of the weight of the silver, if one employs one gram, which is the usual amount in silver determinations.

Thus, in a double decomposition of salts giving a substance as completely insoluble as silver chloride we see that, if we employ the exact quantity of reagent necessary according to the equation of the reaction, we may introduce an error amounting to one thousandth by the fact that the reaction is limited by reverse double decomposition. An equilibrium is established between the three soluble salts, silver nitrate, sodium chloride and sodium nitrate, an equilibrium which is disturbed by the addition of either silver nitrate or sodium chloride, and the work of Mulder has clearly shown that the precipitation of chlorine or of silver is complete only with an excess of the precipitating reagent.

With salts more soluble than silver chloride, the effect of the excess of the reagent is even more pronounced. This is true, in the precipitation of lithium by ammonium fluoride, used by A. Carnot* in his method for the determination of lithium, the author showed that the solubility of lithium fluoride either in pure water or in ammoniacal water is reduced about one half by a slight excess of ammonium fluoride.

This influence of the *excess of the reagent* is well known at present and very generally applied in making the precipitation more complete, and is derived directly from the law of equilibrium in double decomposition of salts. We shall demonstrate it by an

* A. Carnot, *C. R.*, cvii, 237, 336 (1888).

example very frequently employed in analytical chemistry, the precipitation of sulphuric acid by barium chloride:

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

Barium sulphate is very slightly soluble, but its solubility in pure water (one part in 400,000 parts of water or 2 mg. in 5 liters) is far from being negligible. If there is then added to the sulphuric acid just the quantity of barium chloride corresponding to the preceding equation, there will remain in solution a small quantity of barium chloride, sulphuric acid and barium sulphate conforming to the isothermal equation of equilibrium

$$\frac{C^{i}_{BaCl_2} \cdot C^{i'}_{H_2SO_4}}{C^{i''}_{BaSO_4} \cdot C^{i'''}_{HCl}} = k,$$

and consequently, a little sulphuric acid will remain unprecipitated.

Let us now add an excess of barium chloride which increases $C^{i}_{BaCl_2}$. In order that the equilibrium be maintained, it is necessary that $C^{i'}_{H_2SO_4}$ diminish, or that $C^{i'''}_{HCl}$ increase, since $C^{i''}_{BaSO_4}$ cannot increase, the solution being saturated with barium sulphate. Now, in order that the concentration of sulphuric acid should diminish or that the concentration of hydrochloric acid should increase, it is necessary that a new quantity of barium sulphate should precipitate. Thus the excess of the reagent, barium chloride, will render the precipitation of the sulphuric acid more complete. Likewise, if we wish to precipitate all the barium contained in a solution, it will be necessary for the same reason, to add an excess of sulphuric acid.

If, to simplify the discussion, we reduce the equilibrium equation to $\frac{C \cdot C'}{C'' \cdot C'''} = k$, it is clear that in order to diminish C' one half, it will suffice to double C, assuming that the denominator varies only a little; which is clearly true, since the concentration C'' of barium sulphate, being at the point of saturation, may be regarded as constant, and since C''', the concentration of hydrochloric acid, is relatively very slightly increased by the conversion of the last traces of free sulphuric acid into barium sulphate, giving an equivalent quantity of free hydrochloric acid. As the double decomposition between sulphuric acid and barium chloride, taken in equivalent quantities, leaves really only very small quantities of free sulphuric

acid and barium chloride in solution, we see that there will necessarily be required a few milligrams of barium chloride per liter in excess to reduce to negligible traces the initial quantity of non-precipitated sulphuric acid. The more soluble the precipitate the larger must be the excess of the precipitating reagent in order to render the precipitation more complete.

The rôle of the excess of the reagent, however, does not stop with this. It has been known for a long time, in general, that a salt becomes less soluble in water when there is added to it a certain proportion of the acid or base of the salt. Hence the alkali chlorides in saturated solutions are precipitated by the addition of hydrochloric acid or of the alkali of the salt; similarly lead nitrate by nitric acid; barium chloride, by hydrochloric acid; etc. Moreover, it is not always necessary that the acid or the base added be free in order to diminish the solubility of the dissolved salt. They produce an effect in the same direction, although less energetic, added in the form of the salt of another metal, if it is a question of the acid, or of another acid, if it is a question of the base. To bring out, in this case, the diminution of solubility of the dissolved salt, it is necessary to discuss slightly soluble salts. As I have shown, a saturated solution of lead chloride (soluble in 135 parts of cold water) precipitates immediately upon the addition of a few drops of lead acetate or lead nitrate, or of sodium chloride. Likewise, a saturated solution of lead iodide (soluble in 1235 parts of water) precipitates by a few drops of lead acetate or of potassium iodide, while the addition of other salts differing from the salt in solution by acid and by base, produces no precipitation.

The *excess of reagent:* Introducing into the liquid, either in the free state or in the form of a salt, an excess of the acid or of the base contained in the precipitate, has then, in general, the effect of diminishing still more the solubility of the precipitate. If we rely on the preceding equilibrium equation, we see that $C_{H_2SO_4}$ diminishes with the excess of $BaCl_2$, not only by virtue of the law of equilibrium, but also because the value of C_{BaSO_4} itself decreases, which brings about a diminution of $C_{H_2SO_4}$ in order that the equilibrium may subsist.

This additional influence of the excess of reagent is easily explained by hydrolysis.

Let us consider, in fact, a saturated solution of a salt AB, in contact with an excess of the same solid salt. We have present in

the solution, the non-hydrolyzed dissolved salt in equilibrium with the free acid A and base B coming from the dissociated portion.

Free acid + free base ↔ non-hydrolyzed dissolved salt.

Let us apply to this equilibrium the general law, assuming the coefficients i equal and the coefficients $n = 1$, to simplify the reasoning. We have

$$C_A \cdot C_B = kC_{AB}.$$

Introduce into the solution, without modifying its volume, a little of the acid or base of the free salt or in the form of another dissolved salt, more or less hydrolyzed. The state of the system is going to be modified. Let us suppose that we have added acid: we increase C_A. In order that the equilibrium subsist, it is necessary that the product $C_A \cdot C_B$ remain constant, since C_{AB} cannot increase, the solution being already saturated in reference to the salt AB. C_B must diminish then, which can be obtained only by the combination of a certain number of molecules of B introduced with the molecules of A; but, as the solution is already saturated with the non-hydrolyzed salt AB, the molecules AB, thus produced, must become precipitated from solution.

It is easily seen that the diminution of solubility of the salt AB, resulting from this precipitation, will be more perceptible for a small excess of reagent added in proportion as the product $C_A \cdot C_B$ is smaller, that is, for but slightly hydrolyzed salts; chlorides, nitrates and sulphates of the strong bases, on condition, of course, that no special combinations can be produced between the salt AB and the reagent added, as in the case of sulphuric acid added to the neutral sulphate of potassium which produces the bisulphate, more soluble than the neutral sulphate. Hydrochloric acid, for example, added in slight excess to saturated solutions of chlorides, precipitates in a quantitative manner, so to speak,* chlorides of very strong bases: potassium, sodium, barium, calcium, which are very slightly hydrolyzed. With chlorides of medium strong bases (magnesium group), it is only with very strong concentrations of hydrochloric acid that the precipitation takes place (proto-chlorides of iron and chromium); chlorides capable of giving oxychlorides have, on the contrary, their solubility increased by hydrochloric acid ($ZnCl_2$, $SnCl_2$, Fe_2Cl_6).

* Engel, *C. R.*, civ, 433 (1892). These precipitations may be a source of error in quantitative determinations in that they cause one to think, at times, of the formation of salts insoluble in water.

One can then say that, with the exceptions due to the formation of special combinations between the precipitate and the precipitating reagent, the excess of the reagent favors, in general, precipitation by making it more complete. For the same reasons, the solubility of precipitates is diminished in the washing liquid by adding to the wash water the acid or base of the precipitate either free or in the form of a salt. The applications of this principle to chemical analysis are innumerable. For example, the washing of ammonium magnesium phosphate with ammonia water, of potassium fluoborate with potassium acetate in the determination of boric acid by the Stromeyer method, of ammonium phosphomolybdate with ammonium nitrate, lead sulphate with a water slightly acidified with sulphuric acid, mercurous chromate with a solution of mercurous nitrate, etc. One should, of course, choose the additional substance in such a way that it will not interfere in subsequent operations. That is why ammonium or mercury salts are freely employed, which later heating removes completely from the stable precipitates. In certain cases, we can, after the use of a fixed salt, remove the latter by another wash water in which the precipitate may be totally insoluble. It is thus, that, in one of the previous examples, the potassium acetate in the wash water is removed from the potassium fluoborate, by means of alcohol which dissolves the acetate and in which the fluoborate is completely insoluble.

Ostwald's Solubility Product.—Ostwald gave in another form,* the explanation of the influence of the excess of reagent, by basing his statements upon the electrolytic theory and by laying down what he calls the principles of the *solubility product* (*Löslichkeit produkt*). We shall give his demonstration in detail, for we have here a particularly interesting example of the reciprocal relation of the calorimetric and electrolytic explanations.

Let us assume, says Ostwald, a solid electrolyte in contact with a saturated aqueous solution. The solution contains in equilibrium the electrolyte in part undissociated and in part dissociated into its ions. The concentration C of the undissociated part is controlled by the ordinary law of equilibrium of solid bodies in saturated solution in contact with the solid body in excess; it is then constant.

The concentrations a and b of the dissociated parts, ions, are, on the contrary, variable and related to the concentration c of the undissociated part, with which the free ions are in equilibrium by

* W. Ostwald, *Wissenschaftlichen Grundlagen der anal. Chemie,* p. 73.

the ordinary equation $ab = kc$ (if it is a question of monovalent ions), k being constant for a given temperature.* As c is constant for a given temperature, so the product ab is constant. Ostwald calls it the *"solubility product,"* which, for any salt whatever, has always a definite value for a given temperature. If the electrolyte were composed of polyvalent ions in the proportion of m acid ions to n basic ions, the product of solubility would then take the form: $a^m b^n = \text{Const.}$ From this definition, Ostwald formulates the following principle, which is an immediate corollary:

"Each time that in a liquid the product of solubility of a solid substance is exceeded, the liquid is supersaturated in proportion to its solid substance; each time that the product of solubility is not yet attained, the liquid acts as a solvent upon the solid."

By means of this principle, Ostwald easily explains the rôle of the excess of reagent in rendering the precipitation more complete.

Let us assume, for example, that it is a question of the determination of SO_4 in the form of $BaSO_4$ by means of $BaCl_2$. If we add only the quantity of barium chloride exactly the equivalent of SO_4 to be determined, there will remain in solution a proportion of SO_4 ions corresponding to the solubility product of barium sulphate, that is to say, that the concentration a of the SO_4 ions remaining in solution, multiplied by the concentration b of the non-precipitated barium ions, should give a product equal to the constant kc. Let us now add a small excess of barium chloride, then the factor b of the product ab is increased, and as this product should remain equal to kc, the value of the factor a must diminish, which necessitates the precipitation of a new quantity of barium sulphate. Adding again some barium chloride, a new effect will be produced in the same direction; however, the mass of the free SO_4 ions can never become nil, because the concentration of the Ba ions cannot be rendered infinite.

From the solubility product, Ostwald deduces again this rule, that the excess of reagent ought to be greater in proportion as the precipitate is more soluble. In fact, to reduce the concentration of the ion to be precipitated to the nth part of that which it possesses in pure aqueous solution of the precipitate, a quantity of the other ion n times larger must be introduced, and n should be larger in pro-

*Let us observe here that this coefficient k is not the same as in the preceding thermodynamic equation of equilibrium. It is even perceptibly the inverse of what we have said on the reciprocity of hydrolysis and ionization.

portion as the solubility is itself greater. On the contrary, if the precipitate is but slightly soluble, *kc* is necessarily very small and then a small excess of the precipitating reagent suffices, in general, to precipitate practically all of the ions to be determined.

We see that the electrolytic explanation of the influence of the excess of reagent amounts practically to the same thing as the calorimetric explanation which I gave above. The electrolytic explanation, however, does not take into account this fact that, for example, neutral chlorides of strong bases are much more completely precipitated by hydrochloric acid than those of weak bases, and the solubility product tends even to a contrary conclusion, since this product is with equal solubility smaller for a chloride of a weak base than for a more ionized strong base, and that it would consequently seem that the same excess of hydrochloric acid ought to make this product decrease for alkali chlorides less easily than for chlorides of the medium strong or weak bases while in fact it is the contrary that is true.

Substitution of a Weak Acid for a Free Strong Acid in Solution.—This is one of the most frequent operations in analytical chemistry. It has for its aim to permit the formation of a precipitate which would be soluble in a strong acid and consequently would not form in presence of this free acid, while it is insoluble in a weak acid and forms in the presence of the latter, this weaker acid having still sufficient strength to maintain in solution other substances which it is desirable to leave dissolved.

The process permitting the substitution of a weak acid for a free strong acid is derived readily from the heats of neutralization of the same base, sodium hydroxide, for example, by the series of acids, and the stability of the salts formed in presence of water.

The simplest case is that in which two monobasic acids, and of a single property, stand opposed, that is to say, such that each one can form in presence of water only a single compound with an alkaline base. In that case, as we have seen (Chapter III, Section 1), the acid capable of liberating heat by decomposing the neutral salt of the opposed acid is the one which remains combined with the base in a clearly complete manner when the salt which it forms is stable in presence of water. It is thus, then, by adding sodium acetate to a solution containing free hydrochloric or nitric acids, the latter are combined entirely with the sodium, and there no longer remains anything but the free acetic acid.

With exactly equal equivalents, there would remain, of course, a trace of free strong acid; but by adding an excess of sodium acetate it is determined at will, conforming to the equilibrium equation:

$$C_{HNO_3} \cdot C_{\text{acetate}} = k\, C_{\text{nitrate}} \cdot C_{\text{acetic acid}}.$$

It is necessary to notice that, in this case, in common practice in analytical chemistry, a part of the acetic acid liberated by the strong acid, can combine with the sodium acetate in excess in order to give a triacetate. This triacetate (whose formation in the solid state liberates 5.7 Calories) is, however, dissociated practically completely by water, so that, finally there is only free acetic acid.

The neutralization of hydrochloric and nitric acids is likewise practically complete with the formates of the alkalies, and it is always thus when two acids of very unequal strengths are opposed to each other. On the other hand, it is quite different when the acids are of comparable strength; strong monobasic acids opposed to each other, likewise the fatty acids which are not utilized in analytical chemistry; and one can change, for example, a nitric acid solution into a solution containing only hydrochloric acid by repeated evaporations to dryness, after the addition each time of an excess of hydrochloric acid, involving irreversible reactions, such as the formation of nitrosyl chloride, which allows the elimination more and more completely of all the free nitric acid or nitrates.

In the case of the polybasic acids, the effects may be more complicated, because these acids form with the same base several combinations of different stability in presence of water. If the polybasic acid is very weak, as boric acid, it is displaced from its combination with the alkalies completely by strong monobasic acids, as is shown from the calorimetric measurements of Berthelot:

$$\tfrac{1}{2}Na_2B_4O_7 + HCl \text{ (liberates)} + 2.13 \text{ Calories}$$

$$\tfrac{1}{2}B_4O_6 + NaCl \text{ (free)} + 0.08 \text{ Calories}.$$

The difference, 2.05 Calories, is, in fact, almost exactly equal to the difference of the heats of neutralization:

$$13.7 \text{ Calories} - 11.6 \text{ Calories} = +2.1 \text{ Calories}.$$

Sulphuric acid displaces acetic acid completely from sodium acetate in a manner similar to two molecules of a strong monobasic acid.

$\frac{1}{2}H_2SO_4 + NaC_2H_3O_2$ liberates +2.38 Calories,

$\frac{1}{2}Na_2SO_4 + HC_2H_3O_2$ liberates — 0.12 Calories.

The difference, 2.50 Calories, is almost equal to the difference of the heat of neutralization: 2.57 Calories. A sulphuric acid solution can be rendered exclusively acetic by an excess of sodium acetate, exactly similar to the hydrochloric and nitric acid liquids.

Finally, hydrochloric acid displaces in a precisely complete manner, the oxalic acid of sodium oxalate, but with the absorption of a very noticeable amount of heat, as the following data show:

$HCl + \frac{1}{2}Na_2C_2O_4$ liberates — 0.70 Calories,

$\frac{1}{2}H_2C_2O_4 + NaCl$ liberates +0.05 Calories.

The difference, — 0.65 Calories, corresponds exactly to the difference of the heat of neutralization of hydrochloric and oxalic acids by sodium hydroxide.

13.69 Cal. — 14.34 Cal. = — 0.65 Calories.

The last example shows that it is impossible to foresee the direction of displacement by the single consideration of heats of neutralizations when it is a question of acids of different basicities. Perhaps it is the hydrolytic dissociation of normal sodium oxalate into free oxalic acid and sodium binoxalate which would explain, in this case, the direction of the displacement.

The applications of this general method of displacement of a free strong acid by a weaker acid are extremely numerous in analytical chemistry: the precipitation of zinc from an acetic acid solution by hydrogen sulphide, of lead as the chromate from an acetic acid solution, the determination of normal calcium phosphates by the so-called "acetate" method, etc.

Decreasing the Free Weak Acid by the Addition of an Alkali Salt of the Same Acid.—The experience of chemical analysis has shown for a long time that when the precipitation of an insoluble compound is to be made in a solution containing a weak acid or a medium strong one in the free state, capable of keeping the precipitation from being complete, one can succeed in making it complete by adding to the solution a greater or less excess of the normal alkali salt of the free acid. It is in this manner that, as Rivot indicated, the precipitation of nickel or cobalt by hydrogen sulphide, which does not take place in a hydrochloric acid solution, is possible,

but only partial in an exclusively acetic acid solution, and becomes complete if we add to the solution a large excess of alkali acetate. The rôle of the alkali acetate added to the hydrochloric acid solution is not limited then, as in the previously examined cases, to the substitution of acetic acid for free hydrochloric acid. There is in addition, an apparent *decrease* of the acetic acid by the addition of the excess of alkali acetate.

Ostwald gave an explanation of this phenomenon which is certainly one of the most attractive deductions of the electrolytic theory. We will briefly summarize it before giving the calorimetric explanation which we have deduced from the experimental study of these reactions.

Let us assume, says Ostwald,* that we mix in the same solution two electrolytes having a common ion, the acid ion, for example. If the two electrolytes are highly ionized, no notable reaction will be produced by reason of their being mixed. It will be the same if we mix a slightly dissociated electrolyte, a weak acid, for example, with a normal salt of this acid, which itself is highly ionized. In this case, however, there is a forcing back of the ionization of the acid, which is thus weakened, its strength being proportional to the free H ions. This follows from the equilibrium equation $ab = kc$ between the concentrations a and b of the free cations and anions of the acid and the concentration c of the non-dissociated part of the acid. The acid being weak, c is very large in comparison to a and b: if then, we add to the solution a normal salt of the same acid, a is greatly increased, and b (the concentration of the hydrogen ions) ought from that moment to decrease almost in the same proportion, c being able to increase but very little, since the larger part of the acid exists already in a non-dissociated state in the solution. The free acid is then greatly weakened by the addition of the neutral salt, and this weakening will be the more noticeable as the acid is itself weaker, and by the addition of a larger amount of the normal salt.

In support of this theory, Ostwald refers to the following experiments. He shows first the parallelism between electrical conductivity (degree of ionization) and the strength of acids by determining that sheets of zinc of the same size liberate much more hydrogen in unit time, directly after they are introduced into hydrochloric

*W. Ostwald, *Wissensch. Grundlagen der anal. Ch.* p. 63 (3d Eng. Ed., p. 67.—*Editors' Note*).

acid than into acetic acid of the same molecular concentration. Then he shows the decrease in the strength of the acetic acid by sodium acetate, by demonstrating that of two solutions of acetic acid of the same concentration, the one formed with pure water, the other with a solution of sodium acetate, this latter produces with the same sized piece of zinc a much less rapid evolution of hydrogen.

The following series of experiments which I have undertaken with the view of verifying Ostwald's theory, has permitted me to establish the fact that, in the case which concerns us here, namely, the production of a precipitate in the presence of a free weak acid, the apparent weakening of the latter by a neutral salt of the same acid is explained quite simply by the phenomena of chemical equilibrium.*

1. I have first verified if, as Ostwald indicates it, the decrease in the rate of the evolution of hydrogen by the addition of an acetate, in the action of acetic acid on zinc, is indeed in proportion to the ionization of the acetate. With this object I tried successively the action upon the same sheet of zinc, 17 square centimeters area, carefully cleaned before each trial, of normal solutions of different acetates of the same concentration, mixed with the same proportion of pure acetic acid (20 to 40 per cent of acid) and of five drops of the saturated solution of copper acetate to one hundred cubic centimeters of the solution, to allow the continuous evolution of hydrogen. The decomposing apparatus, furnished with a capillary delivery tube, was kept at a constant temperature by immersion in a rapid current of water. Upon each new test, we waited until the liberation of hydrogen became constant, which occurred at the end of five to ten minutes, and estimated from the number of bubbles produced under a constant water pressure above the delivery tube one bubble = 0.036 cc. in the apparatus employed).

Acetic acid dissolved alone in pure water gives at temperatures between 7.5° and 10.1° very concordant results: 9 to 9.5 bubbles of hydrogen per minute. With different acetates added to the acetic acid the results are as follows:

Sodium acetate	4 bubbles (2 experiments)
Manganese acetate	3.9 to 5.5 bubbles
Zinc acetate	0.7 bubble
Nickel acetate	56.0 bubbles

* G. Chesneau, *C. R.*, cxxxviii, 968 (1904).

In the last case a heavy deposit of nickel is formed upon the zinc. With the exception of this last experiment, in which the zinc-nickel couple produced by the zinc deposit enters into consideration, the addition of acetate has clearly decreased the rate of liberation of hydrogen, but not at all in the direction anticipated from the ionization, for manganese acetate, which is certainly less ionized than sodium acetate, produces the same effect as the latter, and zinc acetate, which ought to have about the same ionization as that of manganese acetate,* much more than the latter, and sodium acetate, to the extent of stopping the liberation of hydrogen almost completely. I have, besides, verified the fact that the strength of acetic acid is equally diminished in a very large proportion by *acetone,* whose ionization is absolutely nil, and which, substituted for water to the extent of 50 per cent in the aqueous solution of acetic acid, has reduced the liberation of hydrogen to 0.9 bubble.

This first series of experiments show already at least that it is very difficult to establish a correlation between the rôles played by acetic acid in its action on zinc and in the precipitation of metals of the iron group by hydrogen sulphide.

2. I have afterwards systematically studied the influence of sodium acetate upon the precipitation by hydrogen sulphide, of the metals of the iron group in an acetic acid solution. Ferrous acetate was not tested because of the difficulties caused by the inevitable oxidation of the salt during the experiment. All of the tests were made at the laboratory temperature (on an average of 15°) with the pure acetates of zinc, manganese and nickel in dilute solution. Ten cubic centimeters of a normal or decinormal solution were placed into a conical half liter flask with the addition of definite volumes of pure 40 per cent acetic acid, then, of normal solution of sodium acetate. This was then made up to 250 cubic centimeters with pure water, then 250 cubic centimeters of a saturated solution of hydrogen sulphide were quickly introduced and the flask was

*I have been unable to find any measurements of the electrical conductivity of the acetates of manganese and zinc in the works of the authors who have occupied themselves with determining the coefficients $\alpha = \frac{\mu_v}{\mu_\infty}$ of the different salts. The great analogy of the coefficients found for the salts of zinc, iron and copper, permit me to assume that the acetates of zinc and manganese have a coefficient close to 0.33 which is that of copper acetate, that of sodium acetate being 0.79.

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immediately stoppered with a cork stopper previously coated with paraffine, which was covered to a depth of from 5 to 10 millimeters by melted paraffine so as to insure it being hermetically sealed.

I have ascertained first that the precipitation of zinc acetate (10 cubic centimeters of normal solution) is complete by the next day, even in very strongly acetic acid solutions (up to 25 cubic centimeters) without the addition of sodium acetate. It was then useless to study the influence of this.

With manganese acetate (10 cubic centimeters of normal solution) the precipitation is practically nil even at the end of ten days, under the previously mentioned conditions in the presence of pure water alone. It is still very slight when all the liquid is saturated with hydrogen sulphide; it becomes very abundant, although incomplete, by the addition of one hundred cubic centimeters of a normal solution of sodium acetate saturated with hydrogen sulphide; but the least addition of acetic acid (less than 5 cubic centimeters) in this last mixture prevents completely any precipitation. The action of the sodium acetate is then real, but it can counterbalance partially, however, only the very small quantity of acetic acid coming from the manganese acetate. Under these conditions, the effect produced by the sodium acetate is not susceptible of being accurately measured.

It is with nickel acetate that the decrease of acetic acid by sodium acetate is most easily studied, especially by employing under the above-mentioned conditions, only ten cubic centimeters of a decinormal solution (representing consequently a very dilute solution). In the presence of pure water without acetic acid or acetate, hydrogen sulphide gives an immediate black coloration, but the nickel sulphide formed remains indefinitely in the colloidal solution, passing completely through the filter. With five cubic centimeters of acetic acid at first there is no coloration, but at the end of twenty-four hours a slight precipitate is noticed. The precipitate is no longer produced with 25 cubic centimeters of acetic acid, even by doubling the concentration of nickel acetate.

With the addition of 75 cubic centimeters of normal sodium acetate, the precipitate of nickel sulphide is complete not only in the aqueous solution of nickel acetate, but also in the presence of acetic acid in increasing quantities up to 50 cubic centimeters of acetic acid. It is only with 75 cubic centimeters of acetic acid that the precipitation begins to become incomplete.

I have ascertained, finally, that acetone weakens in no manner the action of the acetic acid in respect to nickel sulphide.

From these different experiments upon nickel acetate, it is evident that one molecule of sodium acetate prevents the formation of nickel sulphide in a solution of acetic acid containing as many as five molecules of the acid. We cannot, moreover, think of explaining the decreasing effect of sodium acetate by the formation of sodium triacetate, which is produced in a small quantity in dilute solution as has been shown by Berthelot.

3. I have, therefore, been led to investigate the question as to whether hydrogen sulphide does not react upon sodium acetate, even in the presence of free acetic acid, to form sodium sulphide notwithstanding the great difference in the heats of formation of the acetate (13.3 Calories) and of the sulphide (7.8 Calories). We have previously seen, in fact, that the hydrolysis of the acetates of the alkalies is clearly shown by calorimetric measurements, and from the moment a little sodium hydroxide is freed by hydrolysis, hydrogen sulphide in very great excess ought to produce sodium sulphide. As nickel sulphide once precipitated becomes readily insoluble even in the strongest acids, one easily understands that, in the equilibrium which is established between hydrogen sulphide, the acetic acid and sodium acetate, there may be produced traces of the alkali sulphide conforming to the equation

$$2NaC_2H_3O_2 + H_2S = 2HC_2H_3O_2 + Na_2S,$$

in order that the precipitation of nickel sulphide be accomplished.

I have in fact verified the production of a small quantity of sodium sulphide in the action of hydrogen sulphide on sodium acetate, even in the presence of quite large quantities of acetic acid, by using, to indicate the presence of sodium sulphide, sodium nitroprussate in fresh solution. This reaction gives, as we know, no coloration with free hydrogen sulphide in solution, and produces, on the contrary, an intense purple coloration with sulphides of the alkalies, even in minute traces, the purple coloration turning to blue, as I have shown, in the presence of a very large excess of hydrogen sulphide in proportion to the sulphide of the alkali. The nitroprussate gives immediately a strong blue coloration in the mixture of aqueous solutions of hydrogen sulphide and sodium acetate. The formation of the alkali sulphide is decreased and is longer in making its appearance *but not suppressed* by the addition of considerable quantities of acetic acid with the respective concentrations employed in the preceding experiments of the precipitation of nickel sulphide.

The characteristic blue coloration of sodium sulphide is seen at the end of about one minute with twenty cubic centimeters of acetic acid, at the end of ten minutes with fifty, and becomes decidedly apparent at the end of 30 minutes when 100 cubic centimeters of acetic acid are employed. I have in addition verified that, under the same conditions, no coloration is produced by the nitroprussate with a mixture of acetic acid and sodium acetate, or with a mixture of hydrogen sulphide and acetic acid. The blue coloration is therefore due to the formation of small quantities of sodium sulphide.

It is then the production of the alkali sulphide in equilibrium between sodium acetate, acetic acid and sodium sulphide that is the veritable cause of the apparent decrease in the strength of the acetic acid and of the more or less complete precipitation of the acetate of the metal, not precipitated in the presence of acetic acid alone under the same conditions; and it is not at all necessary to employ the electrolytic dissociation theory to interpret this phenomenon.

If our explanation is correct, this consequence, in appearance paradoxical, should result, that if we add to the solution of nickel acetate a neutral salt of a strong acid,—like the chlorides or the sulphates of potassium, sodium or ammonium,—the strength of the acetic acid should appear to increase—and consquently the precipitation of nickel by hydrogen sulphide be diminished or completely prevented—by reason of the small quantity of strong acid which should be liberated by the acetic acid in the partition of the strong base between the strong acid and acetic acid, as we have seen in Chapter III (page 56). This is in fact the result we have obtained: the partial precipitation of nickel sulphide which hydrogen sulphide gave in the preceding experiments with ten cubic centimeters of $\frac{N}{10}$ nickel acetate and five cubic centimeters of acetic acid, is completely prevented if a few grams of a chloride or sulphate of an alkali are introduced into the solution.

This apparent increase in the strength of a weak acid produced by the addition of a neutral salt of a strong acid, which had not yet been brought to our knowledge, could be used for certain separations, for example, that of nickel and zinc, whose complete precipitation by hydrogen sulphide is not prevented by traces of free hydrochloric acid.

2. Methods for Bringing into Solution a Compound Insoluble in Water or Acids

This problem, the reverse of precipitation of double decomposition of salts, is one of those which must be constantly solved in the chemical analysis of inorganic compounds. It is employed in a simple form for all the minerals of the metallic sulphides containing silicious gangue, by treating with strong acids, oxidizing, if necessary; the metallic sulphides are dissolved without changing the silica, and by simple filtration the dissolved metals are separated from the insoluble residue.

A more difficult case to solve, which presents itself frequently in chemical analysis, is that in which there is a mixture of several substances equally insoluble in acids, such as silica and the sulphate of barium or of lead. The methods employed in this case are again derived from the law of equilibrium in double decomposition of salts.

We can, according to the case, proceed by two different methods: either transform one of the substances insoluble in acids into another body insoluble in water, but easily decomposed by acids, by Dulong's alkali carbonate method of decomposition, or treat the insoluble substances with a reagent, causing in only one of them a double decomposition from which results only soluble substances.

Dulong Method by Wet or Dry Way.—This method is very general and allows the transformation of the acid of an insoluble salt into a soluble alkaline salt, while the base of the salt passes into the state of a carbonate insoluble in water but easily dissolved by hydrochloric or nitric acids. From these results the possibility of easy determination, after this transformation of the acid and base of the salt, each of them being present in combinations of physical states different and easy to separate by simple filtration.

Let us consider as an insoluble salt, barium sulphate, for example, and let us treat it with a solution of potassium carbonate. This is the equilibrium studied by Guldberg and Waage,

$$BaSO_4 \text{ insoluble} + K_2CO_3 = K_2SO_4 + BaCO_3 \text{ (insoluble)}.$$

We have seen that the transformation of barium sulphate stops when the concentration of the potassium sulphate formed reaches about one fourth of the concentration of the remaining carbonate of potassium conforming with the equilibrium equation:

$$\frac{C^{2.26}_{K_2CO_3}}{C^{2.11}_{K_2SO_4}} = 4 .$$

Then, for a mixture with equal molecules of barium sulphate and potassium carbonate, only about one fifth of the barium sulphate is transformed into carbonate. It is necessary then, in order that the transformation be complete, to take about five molecules of potassium carbonate to one molecule of barium sulphate. In practice, we use sodium carbonate instead of potassium carbonate, because sodium sulphate is much more soluble than potassium sulphate, and we use a large excess of alkali carbonate (10 molecules of Na_2CO_3 to one molecule of $BaSO_4$). Besides, we heat at the boiling point in order to facilitate the reaction, which is endothermic and favored consequently by an elevation of the temperature, conforming to the principle of opposition of action and reaction. It is well, for the same reason, to make the filtration while the liquid is hot. The reaction is, moreover, slow, because it takes place between substances of different physical states, of which one, the barium sulphate, is almost absolutely insoluble.

If one has quartz mixed with barium sulphate, as it is not attacked by boiling sodium carbonate, it will be sufficient to filter the residue, and, after washing, treat the mixture with a dilute acid, hydrochloric or nitric, to dissolve completely the barium carbonate and leave the insoluble quartz.

The same transformation of an insoluble carbonate, with transformation of the acid of the salt into soluble alkali salt, can be accomplished by the *dry method* as well as by the *wet method,* by heating to the fusion point at a bright red heat, the mixture of insoluble salt and of sodium carbonate in excess, or better a mixture of equal equivalents of potassium carbonate and sodium carbonate, whose fusion point is lower than the fusion points of the separate salts. The theory of the dry method is the same as that of the wet method and it is the respective concentrations of carbonates and alkali sulphates united in a homogeneous mixture which control the equilibrium in this case.

But in the dry method, another factor is to be considered, that of the stability of the carbonates of the metals formed at the fusion point of the alkali carbonates. Since starting with calcium, all the carbonates are easily dissociated by heat at the fusion temperature

of the carbonates of the alkalies, it is generally an oxide which is produced instead of a carbonate, with the liberation of carbon dioxide, and, if this oxide has the function of an acid (Al_2O_3 for example), it forms with the alkali a product generally soluble in water. But the problem is, however, greatly simplified, for it is sufficient then to produce in the solution obtained, the precipitation of one of the substances by an appropriate method. This is the case in the separation of silica from aluminium in clays, by fusing with an alkali carbonate, dissolving the soluble silicate and aluminate of the alkalies formed in water, then precipitating the silica by hydrochloric acids, etc.

Redissolving an Insoluble Substance by a Suitable Reagent.—In many cases, a salt formed of a weak acid and insoluble in water, can be dissolved by means of a stronger acid, whenever this latter can give a soluble salt with the base of the salt. Calcium oxalate or phosphate, insoluble in water, are immediately transformed by hydrochloric acid, into soluble calcium chloride and oxalic acid or phosphoric acid in apparent opposition to the laws of Berthollet. The reaction is indeed a reaction of equilibrium, but in which, by reason of the great evolution of heat, the transformation of the system is practically complete, as we have seen in Chapter III, Section 3.

In many cases, however, where one fails with a strong acid, he can frequently succeed in getting into solution an insoluble salt with a neutral soluble salt, which may present a certain advantage over the use of acid reagents. Thus, for example, in treating lead sulphate which is insoluble not only in water, but also in quite strong acids, with an alkali salt of a weak acid, as sodium or ammonium acetate, it is easily redissolved, and one can by this method, separate easily the lead sulphate obtained from action of oxidizing acids on galena, from the siliceous gangue frequently accompanying these minerals.

This action, in appearance paradoxical, is a direct consequence of the law of equilibrium in the double decompositions of salts. The reaction

$$PbSO_4 + 2NaC_2H_3O_2 = Na_2SO_4 + Pb(C_2H_3O_2)_2$$

23.8 Cal. 26.6 Cal. 31.4 Cal. 15.5 Cal.

is in fact an equilibrium reaction limited by the reverse reaction. The direct reaction is produced with the absorption of heat (— 3.5

Calories), but the proportion of the first system transformed into the second is hardly appreciable with an equimolecular mixture. It is the predominating stability of the sodium sulphate in the aqueous solution which is the determining cause of the reaction. It is sufficient then to greatly increase the concentration of the sodium acetate in order that the concentration of sodium sulphate and of lead acetate controlled by the equation:

$$C^{2i}{}_{NaC_2H_3O_2} = k\, C^{i'}{}_{Na_2SO_4}\, C^{i''}{}_{Pb(C_2H_3O_2)_2},$$

attain the value corresponding to the complete solution of the lead sulphate. The following are the quantities of this substance which are dissolved by the sodium acetate at different concentrations, according to H. C. Debbits:*

Sodium Acetate in 100 Grams of Solution	Lead Sulphate Dissolved
2.05 grams	0.054 gram
8.20 "	0.900 "
41.00 "	11.200 grams

Heat increases, moreover, the solubility, the thermal sign of the reaction being negative.

For reasons of the same kind, one must use discretion in allowing the presence of perfectly neutral additional salts, in liquids in which a definite precipitate is sought, for the preceding example shows that this precipitate may become incomplete by reason of the presence of these salts, which might seem *a priori* to be without effect.

The study of every method of analysis employing an insoluble precipitate ought to be made with special attention to the action upon this precipitate of all reagents which might be present in the solution at a given moment in the course of the analysis. The failures that are met at times in the use of a method, come from the fact that this method was established by its author while using exclusively pure reagents destined to produce the desired reaction, while in practice the disintegration of the one often necessitates the introduction into the solution of a considerable quantity of foreign substances (salts of the alkalies, acids, etc.). Hence, while the presence

*H. C. Debbits, *Bull. Soc. Chim., Paris* (2) xx, 258 (1873).

of even a quite considerable excess of hydrochloric acid does not prevent the precipitation of sulphuric acid by barium chloride, care must be taken not to cause this precipitation in the presence of free acetate of the alkalies which produce upon barium sulphate an action (less, it is true) analogous to that which they have with lead sulphate. In this case, it will be sufficient to make the solution decidedly acid with hydrochloric acid to destroy the sodium acetate and to free the acetic acid which is without action upon barium sulphate.

For analogous reasons, the precipitation of sulphuric acid by barium chloride is incomplete in the presence of copper salts or of magnesium. On the other hand, it is not perceptibly interfered with by the presence of zinc salts; and it is sufficient, for example, to precipitate copper from its solution by zinc to be able afterwards to determine quite accurately the sulphuric acid present.*

3. Precipitates of Variable Composition

The principles which we have previously given suffice, in general, to explain and direct the methods of analysis based upon double decomposition of salts, each time that the latter causes only a slight precipitate of invariable composition in equilibrium with the reagents remaining in solution even while varying within quite wide limits of temperature and respective concentration. Such are the cases of the precipitation of hydrochloric acid by silver nitrate, which gives only silver chloride; of sulphuric acid by barium chloride, which gives only barium sulphate, etc., as well hot as cold, and in liquids more or less strongly acid.

It is not the same, however, when, according to the conditions of temperature and concentration there may be produced several different precipitates, either pure simple salts or mixtures, in equilibrium with the solution.

These variations in the composition may affect either only the degree of hydration or the respective proportion of the acids and bases.

Hydrates of Variable Composition.—The first case is very frequent in analysis: many metallic hydroxides, sulphides, certain insoluble salts, as calcium oxalate, oxides with acid properties: metastannic, titanic, silicic, etc., have different degrees of hydration according to the temperature at which they are precipitated. If

* G. Chesneau, *C. R.*, cxxxvii, 653 (1903).

one were satisfied with weighing them after drying on a tared filter, he would have quite uncertain results varying from one experiment to another. In general, however, this uncertainty as to the degree of hydration is easily removed by transforming the precipitate into an anhydrous substance of very constant composition, for oxides and the oxidized salts by simply igniting, for sulphides by heating in an atmosphere of sulphur or a current of hydrogen sulphide.

Double Ammonium Salts: Quantitative Determination of Arsenic and of Phosphorus.—It is different, however, when the relative proportions of bases and acids vary in the precipitate with the factors of equilibrium. The precipitates in the form of insoluble double ammonium salts belong generally to this category. The determination of arsenic in the form of ammoniacal arsenate of cobalt (method of O. Ducru) and of phosphorus in the form either of ammonium magnesium phosphate or of ammonium phosphomolybdate offer very striking examples of these variable compounds.

Concerning the precipitation of arsenic in the form of ammoniacal arsenate of cobalt produced by the action of cobaltic chloride upon arsenate of ammonium in the presence of ammonium chloride, and of free ammonia and prolonged digestion of the precipitate in the mother-liquor, the author* of the method, has shown that according to the concentration of ammonia, which influences only the composition of the precipitate, it varies in a continuous manner with the concentration of ammonium hydroxide from natural erythrine $Co_3(AsO_4)_2+8H_2O$ to $Co_3(AsO_4)_2 \cdot 3NH_3+5H_2O$, NH_3 replacing the water molecularly, as the following diagram shows. The abscissas represent the concentration in free ammonia expressed in

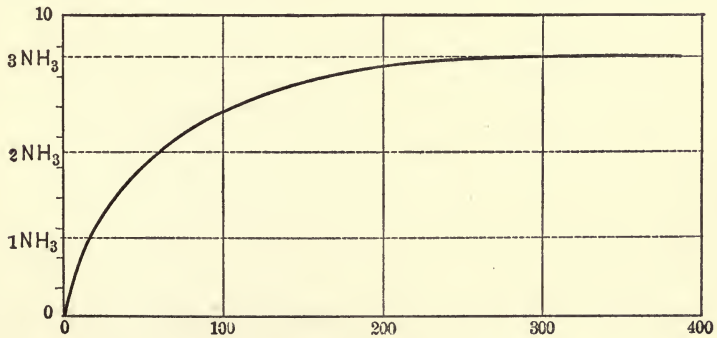


FIG. VI

* O. Ducru, *Thèse de doctorat,* and *C. R.,* cxxxi, 675, 886 (1900).

cubic centimeters of ammonium hydroxide of a density of 0.921 per liter of solution and the ordinates the contents of the salt in per cent of NH_3. It is indeed a question here, as the author has shown, of a veritable chemical equilibrium between the solution and a complex precipitate, which appears in addition to be a homogeneous solid, for the different ammonium arsenates of cobalt are isomorphous and consequently form a solid solution. It is then impossible to obtain a precipitate of an exact fixed composition, but this variation presents no difficulty because, by reason of a wholly fortuitous circumstance, NH_3 and H_2O having almost the same molecular weight, the content of arsenic in the precipitates does not vary perceptibly whatever may be the proportion of water displaced by ammonia in the precipitate.

The methods for the quantitative determination of phosphorus unfortunately do not present the same peculiarities.

In the precipitation of phosphoric acid in the form of ammonium magnesium phosphate, by magnesium chloride in the presence of ammonium chloride and ammonium hydroxide, there may be produced, depending on the concentration of the ammonium hydroxide either trimagnesium phosphate, $Mg_3(PO_4)_2{\cdot}5H_2O$, or $MgNH_4PO_4{\cdot}6H_2O$, and we generally have a mixture of the two at the beginning of the precipitation. Here it is very necessary to have as the final product the second compound only, to obtain after heating the well-defined pyrophosphate $Mg_2P_2O_7$ and not a mixture of $Mg_2P_2O_7$ and $Mg_3(PO_4)_2$, which have quite different contents of phosphorus. From the investigations of H. Lasne* it is the presence of greater or less proportions of tri-magnesium phosphate in the final product which explains the variations, often very appreciable, obtained in the analysis of the same phosphate. The use of strongly ammoniacal solutions (one-third of the volume concentrated ammonium hydroxide) seems to prevent this error, as H. Lasne indicates, for trimagnesium phosphate redissolves little by little in the ammonium hydroxide and then reprecipitates slowly in the form of ammonium magnesium phosphate. If one filters too soon there may be even after two or three hours of digestion, enough tri-magnesium phosphate to make the error of the content of phosphorus 0.4 per cent, and the digestion should be prolonged for sixteen hours at least.

The precipitation of phosphoric acid in the form of ammonium

*H. Lasne, *C. R.*, cxxvii, 62 (1898).

phosphomolybdate, which is the only known method for the very accurate quantitative determination of phosphorus in cast irons or steel, presents sources for error of the same kind. It is known from the early investigations of Svanberg and Struve* that, if a solution of phosphoric acid or of a phosphate is poured into a large excess of nitric acid solution of ammonium molybdate, $7\ MoO_3 \cdot 3(NH_4)_2O \cdot 4H_2O$, there forms slowly in the cold, rapidly when hot, a yellow crystalline precipitate containing all the phosphoric acid, with ammonium hydroxide and an enormous quantity of molybdic acid, nearly thirty times the weight of the phosphoric acid. Sonnenschein,† who first applied this method to the quantitative determination of phosphorus, fearing that this yellow substance might not be a definite compound by reason of this very high ratio, recommended its dissolution in ammonium hydroxide and the reprecipitation of the phosphorus in the form of ammonium magnesium phosphate. The advantage of having a precipitate much heavier than the element to be determined, very important for determining traces of phosphorus, was thus lost, and a number of workers have sought for the necessary conditions to obtain an exactly definite phosphomolybdate.

H. Debray, who has made a special study of phosphomolybdic acids,‡ obtained several hydrates of an acid to which he assigned the formula, $P_2O_5 \cdot 20MoO_3$, giving in a nitric acid solution containing ammonium nitrate the familiar yellow precipitate, to which he assigned the formula $3(NH_4)_2O \cdot P_2O_5 \cdot 20MoO_3 \cdot 3H_2O$, containing 1.918 per cent of phosphorus.

Debray has, moreover, ascertained that this phosphomolybdate is stable only in the presence of an excess of nitric acid, and that alkalies transform into ordinary molybdates and phosphomolybdates of another phosphomolybdic acid, $P_2O_5 \cdot 5MoO_3 \cdot 3H_2O + Aq$, giving alkaline phosphomolybdates which crystallize into but slightly soluble white needles.

Since the work of Debray, the question of the constancy of the composition of Sonnenschein's precipitate has been frequently studied by reason of its great importance in the metallurgy of iron. The following are the results of the principal authorities:

* Svanberg and Struve, *Ann. de Millon et Reiset* (*Annuaire de Chimie*) 1849, p. 163.

† Sonnenschein, *Journal prakt. Chem.*, liii, 343 (1851).

‡ H. Debray, *C. R.*, lxvi, 702, 732 (1868).

Author	Formula	Percentage of P.
H. Debray	$3(NH_4)_2O{\cdot}P_2O_5{\cdot}20MoO_3{\cdot}3H_2O$	1.918
Rammelsberg	$3(NH_4)_2O{\cdot}P_2O_5{\cdot}22MoO_3{\cdot}12H_2O$	1.684
W. Gibbs	$5(NH_4)_2O{\cdot}2P_2O_5{\cdot}48MoO_3{\cdot}16H_2O$	1.597
A. Carnot	$3(NH_4)_2O{\cdot}P_2O_5{\cdot}24MoO_3{\cdot}3H_2O$	1.628

The differences are, as we can see, very considerable.

Since the work of A. Carnot,* it is assumed in the metallurgical laboratories that, by following strictly the method employed by the author, the composition of the precipitate obtained in strong nitric acid solutions at 40° and then dried at 100°, always corresponds to 1.628 per cent of phosphorus, and the numerous verifications made of the synthetic mixtures† prove this. The precipitates of Debray and of Rammelsberg probably contain a little phosphomolybdate with $5MoO_3$ (whose spontaneous production I have at times obtained during the acidifying of the ammoniacal solution of the yellow precipitate). That of Gibbs possibly contains a certain proportion of the white ammonium molybdate which is deposited spontaneously by the molybdate reaction when it is heated. This makes at least three distinct compounds which can be produced in the precipitation of phosphoric acid by a nitric acid solution of ammonium molybdate. We see from these examples how desirable it would be, in all cases where the double decomposition of salts is capable of giving precipitates with variable composition, to determine the limits of concentration of the reactions among which one is sure to obtain a precipitate the composition of which is scientifically certain.‡

Use of the Phase Rule.—The solution of this problem, which is of so great a practical interest, has not been approached in a systematic manner in analytical chemistry. This could be done by applying to precipitates formed in the double decomposition of salts the methods of research employed by Van't Hoff, Backuis Rooze-

* A. Carnot, *Ann. des Mines,* (9) iv, 5 (1893).

† Goutal, *Congrès de Chimie appliquée à Berlin,* ii, p. 8 (1903).

‡ The subject of the precipitation of phosphorus as the phosphomolybdate has been presented in an extensive article by Gunner Jorgensen entitled *Uber die bestimmung Der Phosphorsaure Mémoires de l'Académie Royale des Sciences et des Lettres de Danemark* (7) ii, 141-238 (1905), and more recently by the author, M. G. Chesneau, in *Etude sur le dosage ponderal du phosphore sous forme de Phosphomolybdate d'ammoniaque Revue de Metallurgie,* v. 237-269 (1908).—*Editors' Note.*

boom and the chemists of their school, in the study of the different crystalline precipitates which may be formed, in solutions containing one or more salts in solution, depending upon the concentration and temperature.

We know, thanks to the use of the *Phase Rule* of Willard Gibbs, that these investigations have been able to determine the limits of concentration of the dissolved salts to which the deposit of a definite salt in equilibrium with the solution corresponds. If we represent these concentrations on the axes of a system of coördinates suitably chosen, we obtain for each deposit a definite surface, and the intersections of these surfaces cut out in each of them the *zone* of concentration giving to the state of equilibrium a single definite deposit; along the intersecting lines, the concentrations are such that the liquid is in equilibrium with the deposit formed of two salts which may co-exist in all proportions.

These intersecting lines correspond in double decomposition of salts to the precipitates with variable composition which may be formed by the reagents used, taken under certain concentrations, and what it would be important to determine are the zones of concentrations which can cause only a simple precipitate, *a single solid phase,* consequently a body of an accurately defined composition. [A single solid phase may be a solid solution.—*Editors' Note.*]

Briefly, the way that the application of the phase rule can be made to double decomposition of salts is herein presented. We know that, from this law, if we call C the number of independent components of a system in chemical equilibrium; and P that of the phases* (distinct homogeneous masses into which it is divided); then the form of the law of equilibrium of the chemical system depends exclusively on the number, $C+2-P=V$, which Gibbs terms the *variance* of the system; and which is simply the number of independent variables of the system in equilibrium. In particular, for double decomposition of salts by the method, where the only variable factors are pressure, temperature, and concentration of the substances in solution, the variance is five, if no precipitate is formed. We have, in fact, four salts in solution, hence five constituents including water (or the solvent, whatever it may be from the moment that its elements do not coöperate in the reaction†) on the condition

* For definition of terms, etc., see *The Phase Rule and its Applications* by H. Findlay.—*Editors' Note.*

† If the solvent contains one or more substances which through sharing

that the two salts of the system opposed to the initial system be in equivalent quantity. There are then only four independent constituents, the solvent included and a single phase; the degree of variance is then, five, and the law which governs the equilibrium of the system is then of the form $f(p, t, s_1, s_2, s_3, s_4,) = 0$, calling s_1, s_2, s_3, s_4 the concentrations of each dissolved salt in the ratio to the solvent. If one of the substances of the system reaches saturation and is precipitated, there is one extra phase, and the system becomes *quadrivariant*. This is the usual case of double decomposition of salts giving a single well-defined precipitate, as for any system with four components existing in two phases, where we have $C = 4$, $P = 2$ in which $V = C - 2 - P = 4$. The law which controls the equilibrium is then of the form $f(p, t, s_1, s_2, s_3) = 0$, calling s_1, s_2, s_3, the concentrations of the three salts in solution. For a given value of pressure and temperature, this quadrivariant system can be observed in equilibrium, but the composition of the two phases is not determined entirely with these two data; the concentrations s_1, s_2, s_3, of the three salts in solution can take an infinite number of different values, without dissolving the precipitate and without allowing a new mass of substance to deposit. It is, therefore, necessary, in addition to the pressure and temperature, to assume arbitrarily the values for two of the concentrations so that the third may be determined. It is precisely this law which has been established by the principles of thermodynamics and which is in the form

$$\frac{S_1{}^{n_1{}^i}\, S_2{}^{n_2{}^i}}{S_3{}^{n_3{}^i{}_3}} = k,$$

k being a function of the pressure and temperature.

We can represent the phenomena, at constant temperature and

directly in the reaction, influence the solubility of the precipitate, these substances form, of course, so many extra independent constituents and increase so much more the degree of variance of the system. It is necessary, then, in the reasoning which follows, to assume that a constant concentration be given these substances, so that the solvent figures only for a single constituent. The complete study of double decomposition of salts requires then that a series of constant values be given to the concentration of these bodies, conveniently selected (for example, to that of nitric acid in the solution in which there is to be produced the double decomposition between the ammonium molybdate and the phosphoric acid or to that of ammonium, in the double decomposition between ammonium phosphate and magnesium chloride).

pressure, by a surface referred to three axes of coördinates upon which are plotted the concentrations of the three salts in solution, in equilibrium with the precipitate. As the origin corresponds to the pure solvent, the points situated between the origin and the points of the surface belong to unsaturated solutions of the precipitate, and which will dissolve from it until equilibrium is re-established. The points situated on the other side of the surface with reference to the origin, will be capable of depositing a precipitate.

There will be as many distinct surfaces S, S′, S″, etc., as there are different precipitates C, C′, C″, etc., which the mixture is capable of depositing, each of the zones included between the intersecting lines of the surfaces between them corresponding to *the area* of a distinct precipitate. Along the intersecting lines of the surfaces, the system becomes *trivariant,* since the precipitate is composed of two distinct substances, and the solution can remain in equilibrium with two precipitates. The point of intersection of two lines corresponding to a divariant system for which the precipitate, formed from three distinct substances, would be in equilibrium with a solution no longer containing anything but a substance in solution whose concentration is entirely determined for a given value of pressure and temperature, as in the ordinary case of a saturated solution of a single salt in contact with this salt in the solid state.

To determine the areas of each distinct precipitate, it is sufficient then to ascertain the composition of the precipitates obtained by varying methodically the concentrations. As long as it remains constant, the points corresponding to the concentrations used are in the area of the corresponding precipitate; if it varies, it is because we have passed from one area to another, crossing the intersecting line of the two corresponding surfaces, and this certain result of the phase rule enables the determination by degrees of these intersecting lines giving the boundaries to the area of each distinct precipitate.

This kind of research would be more difficult for double decomposition of salts with insoluble precipitates utilized solely in chemical analysis, than in the classic systems studied by Van't Hoff, Meyerhoffer and Donnan, with the object of explaining the conditions under which the salt deposits of the Stassfurt beds were formed, such as the mixture: water, potassium chloride, magnesium sulphate and magnesium chloride, in which is involved the reaction

$$MgSO_4 + 2KCl = MgCl_2 + K_2SO_4.$$

In such a system, the numerous anhydrides or distinct hydrates, which can be deposited, are, in fact, well crystallized, and the mineralogical examination of the deposit aids greatly in the determination of its nature.

The same characteristics cannot serve for insoluble precipitates, which are, in general, opaque, with amorphous appearance or in the crystalline grains too fine for applying the methods of mineralogical examination, and the analysis of the precipitate would be, in general, the only method available. But, however laborious may be the determinations of these areas of precipitates with a definite composition, it is not unrealizable, and the great importance which it has for fundamental analysis in metallurgy will, doubtless, as a result, cause industrial laboratories to devote to this kind of researches the large amount of work which they require. In any case, it has not seemed useless to us to indicate here the direction in which they should be followed to give to certain methods of analysis an unquestionable scientific basis

CHAPTER VII

STUDY OF SOME METHODS BASED ON DOUBLE DECOMPOSITION OF SALTS

The principal types of methods of analysis based on double decomposition of salts are the volumetric methods by precipitation or by neutralization and the gravimetric methods by precipitation, either by means of reagents producing decomposition with a salt contained in the solution to be analyzed or by simple hydrolysis. We are going, for each of these classes, to show in a general way what are, according to the principles previously established, the points to be discussed in the methods of analysis, then apply this method of examination to a definite example.

1. Volumetric Methods

It would seem that reversible reactions could never serve for volumetric methods, for if we consider the reversible reaction: $AB+A_1B_1 \leftrightarrow AB_1+A_1B$, A_1B_1 being the solution titrated against the solution of the substance AB, the general law of equilibrium, $C \cdot C' = kC'' \cdot C'''$, indicates that theoretically there is no limit assigned to the concentration C of the reagent so that the reaction may be complete. Experiment, however, shows that a large number of reversible reactions are accomplished in a manner *practically* quantitative, that is, the mixture of one equivalent of the second substance with one equivalent of the first gives a reaction sufficiently complete so that a very small excess of the reagent added to the system produces a marked visible phenomenon, which results either from the appearance of a precipitate or from one having just ceased to be produced, or from a sudden change of color due to a special indicator added to the system. This case presents itself when the maximum concentration of one of the bodies of the second system has an extremely small value.

Methods by Precipitation.—Here there is no longer, as in the volumetric methods based upon irreversible phenomena, the slowness of reaction which produces the relative error, since the reaction in the simple double decompositions of salts is almost instantaneous.

It is the difference $\propto$ between the volume of that titrating solution corresponding to the theoretical equation and the volume introduced in order to cause the disappearance or appearance of the precipitate which represents the experimental error. In certain cases, this difference $\propto$ may be very small if the precipitate is very slightly soluble in the mother-liquor. The solubility is slight in the titration of silver nitrate by means of sodium chloride by the Gay-Lussac method, $\propto$ corresponding, according to Mulder, as we have seen (Chapter VI., Section 1), to one milligram of silver for one gram of silver dissolved in the nitric acid.

A rather small error does not exceed in certain cases the order of those of the gravimetric methods; it can, however, be decreased—and that becomes necessary when the difference is large—in the same manner as for the volumetric methods using irreversible reactions (Chapter II., Section 3). In that case it is sufficient to standardize the liquid employed as a reagent not by dissolving a definite weight of the reagent in one liter, but by titrating the solution of the reagent against a solution of a definite weight P of the substance to be determined, taken at a concentration practically equal to that which it possesses in the solution to be analyzed, containing a weight x of the unknown substance. As the difference $\propto$ represents, really, the maximum solubility of the precipitate in the mother-liquor, this difference will be the same if there is little difference between the volumes V and V′ of the standard liquid introduced until the reaction is apparently complete, the first in the liquid to be analyzed and the second in the solution containing the weight P.

Since the quantities of the standard solutions corresponding to the theoretical equation are $V - \propto$ and $V' - \propto$, we will then have

$$\frac{x}{P} = \frac{V - \propto}{V' - \propto} \quad \text{or} \quad x = P\,\frac{V - \propto}{V' - \propto}.$$

The error introduced by taking $x = P\frac{V}{V'}$ is very small, even if $\propto$ represents a notable fraction of $\frac{V}{V'}$. The difference between the relative value x_1 and the true value x is, in fact, assuming $P = 1$:

$$x_1 - x = \frac{V}{V'} \quad \frac{V - \propto}{V' - \propto} = \propto \frac{V' - V}{V'(V' - \propto)}.$$

By disregarding the denominator $\propto$ in respect to V′, we have,

$$x_1 - x = \propto \frac{V' - V}{V'^2} .$$

We see then that, if V and V′ have very similar values, as we have assumed, the error of determination will represent only a very small fraction of $\propto$, while it would be equal to $\frac{\propto}{V}$ by simple titration. In the Gay-Lussac method particularly, it permits results of a precision at least equal to the most exact gravimetric methods.

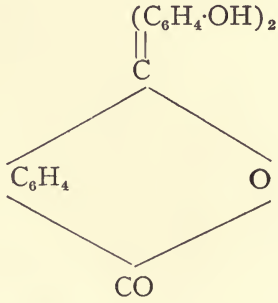
Methods of Neutralization: Acidimetry and Alkalimetry.— When the reaction employed does not indicate by itself a very sudden visible phenomenon at the end of the reaction, it is necessary to employ an additional substance playing the rôle of *indicator.* The typical example of methods with a special indicator is given by the methods of *alkalimetry* and *acidimetry,* in which the quantity of free alkali contained in the solution is determined by exact neutralization by means of a standard acid and reciprocally. As the precise point of neutralization is not indicated by any apparent phenomenon, there is employed an additional indicator having a very different color according as there is an excess of alkali or of acid. It is necessary, however, to occupy oneself particularly with the influence which the hydrolytic dissociation of the salt formed on the one hand, by the alkali and the reacting acid, and on the other, by the compounds formed from the indicator, can exercise upon the definite appearance of the (color) phenomenon in question. The nature of the substance serving as an indicator, as well as the acid or base used in the standard solution, is very important for the accuracy of the determination, and it is necessary to specify the rôle played by each of them in order to make a judicious choice in each particular case; such as the alkalimetry of a strong, medium or weak base, the acidity of a weak, medium or strong acid.

The theory of colored indicators which we shall give only for alkalimetry and acidimetry* can be repeated identically for the *separate indicators* used *by the touch method,* making the double decomposition with one of the coëxisting salts in the reaction used for the volumetric method under consideration.

* This theory has been presented by W. Ostwald (*Wissensch. Grundlagen der anal. Chem.* p. 117) being based entirely upon the ionization of salts; the one we present here is based upon the thermochemical data and the hydrolysis of salts in solution and has its origin in the principles set forth by Berthelot in his *Thermochimie* (*Les lois numériques,* I, p. 356 and following, 1897).

In order that a coloring substance may be employed as an indicator in acidimetry and alkalimetry, it must necessarily be itself of acid or basic nature, without which it would be indifferent to the excess of acid or base reagent. In fact, the principal indicators employed in acidimetry and alkalimetry, litmus, phenolphthalein, and methyl orange or helianthin A, are organic acids of medium or weak strength, that is to say, liberating a medium or small amount of heat of combination with strong bases.

The strongest of the three is helianthin, which is displaced from its combinations with potassium only by acids liberating more than twelve Calories; the weakest is phenolphthalein, analogous in strength to phenol, which liberates eight Calories by combining with strong bases, and finally, litmus contains a mixture of several acids designated under the name of *litmus acid,* intermediate in strength between the two preceding. Phenolphthalein is a colorless acid with the formula



whose alkaline salts are bright pink. Litmus acid exists in litmus in the form of alkaline earth salts: the free acid is red and the salts with strong bases are blue. The commercial helianthin, with the formula

$$C_6H_4(NaSO_3)_4N_1{:}N_1C_6H_4N_4(CH_3)_2,$$

is a sodium salt whose acid is red when free while its alkaline salts are pale yellow.

In the presence of weak bases, these acids give salts more or less hydrolyzed in aqueous solution and their color is consequently intermediate between that of the free acid and the alkali salt. The greater or less degree of clearness with which these indicators mark the exact point of neutralization and consequently their choice in

each definite case, depends upon the principles controlling the stability of salts in aqueous solution (Chapter III., Section 1), namely:

1. Salts formed from a strong base and a strong acid offer a degree of hydration practically nil,—salts from a strong acid and a weak base or *vice versa,* a clearly marked degree of hydrolysis,—salts from a weak acid and a weak base, almost total hydrolytic dissociation.

2. In an aqueous solution, containing several bases and acids of very different strengths, in equivalent quantities, it is the salt least dissociated (hydrolytically) by water (i.e., formed of the strongest bases and acids) which is always produced, weak bases and acids being liberated by hydrolysis (and by double decomposition.—*Editors' Note*).

The first condition then, to be fulfilled by the colored indicator, a body with an acid property, is to be *weaker* than the acid reacting with the base; and it is further necessary, in order that the end point be distinct, that the difference between the heats of neutralization of the reacting acid and the indicator, by alkalies, be quite large. Otherwise, either the indicator will remain in combination with the base and there will be no marked end point; or there will be a partition of the base between the reacting acid and the indicator, and the end point will be *progressive* instead of being sharp.

This being assumed, let us examine first what are the reacting acids and the indicators to be employed in *alkalimetry* (saturation of a base by a standard acid solution), according to the strength of the base.

It will be necessary always to choose by preference a very strong reacting acid, so as to obtain a salt as slightly hydrolyzed as possible, and to liberate the indicator from its combination with the base, by the least possible excess of the reacting acid. On the other hand, the indicator must form with the base a salt without appreciable hydrolysis, or else there will be a progressive end point, since the acid of the indicator would be already in part free before the end of the neutralization.

With strong bases, like potassium hydroxide and sodium hydroxide, we can then employ either of the three above-mentioned indicators by using a very strong acid (HCl, H_2SO_4). We can also take in this case a medium strong acid, as oxalic acid; but then it is necessary to use phenolphthalein as an indicator, since helianthin, an acid almost as strong as oxalic acid, gives an indistinct end point

with this acid. With weak bases, one must use a very strong reacting acid, and the strongest acid indicator, the helianthin.

Let us consider now the conditions to be realized in *acidimetry* (neutralization of an acid by a standard alkali solution). For reasons similar to the preceding, one should employ in general, as strong bases as possible, stronger in proportion as the acid is weaker, and an indicator of as weak acidity as possible, phenolphthalein, since we saw that in all cases the acid to be titrated ought to be stronger than the indicator. When it is a question of titrating very strong acids (HCl, HNO_3, H_2SO_4), bases of only medium strength, like ammonium hydroxide, could be used, with any one of the three indicators, but with medium strong or weak acids, recourse must necessarily be had to potassium hydroxide or sodium hydroxide, with phenolphthalein as indicator. For this reason acetic acid cannot be accurately titrated by ammonium hydroxide, while the end point is very clear with potassium hydroxide and phenolphthalein as indicator.

We may summarize this thus:

1. Helianthin A, a medium strong acid, serves especially for alkalimetry, even for weak bases.

2. Phenolphthalein, a very weak acid, is not suitable for alkalimetry, especially if it is a question of neutralizing weak bases, but answers very well for acidimetry, even with weak acids.

3. Litmus, intermediate in strength between the preceding two, suits neither alkalimetry with weak bases nor acidimetry with weak-acids. It is especially employed in the neutralization of strong bases by strong acids (up to acetic acids, exclusively) and for neutralization of very strong acids by strong or medium strong bases (up to ammonium hydroxide inclusive).

These considerations enable one to understand why salts of weak bases (hydroxides of iron, zinc, copper, etc.,) are not *neutral* to litmus, even when they are formed with a strong acid (hydrochloric, sulphuric), but color the litmus red, even in the presence of an excess of metallic hydroxide. This comes from the fact that the hydroxide is incapable of forming with the acid of litmus a non-hydrolyzed salt; thus, if even a few drops of potassium hydroxide are added to a solution of zinc sulphate, up to the beginning of the precipitate of the zinc hydroxide, the litmus retains a violent red tint. It is not the same with helianthin and phenolphthalein, which are more clearly defined as to strength than litmus, and concerning the zinc hydroxide

whose heat of neutralization by sulphuric acid is 11.7 Calories per equivalent. Zinc sulphate to which phenolphthalein is added remains colorless, and if potassium hydroxide is added it turns red only at the exact moment that all of the sulphuric acid of the zinc sulphate is saturated with potassium hydroxide, the precipitated hydroxide of zinc not being able to form traces of non-hydrolyzed salt with the phenolpthalein. If a few drops of red helianthin be added to zinc sulphate, the solution becomes yellow at the first addition of potassium hydroxide, because the basicity of the zinc hydroxide displaced by the potassium hydroxide is sufficient, so that the helianthin,—a stronger acid than the acid of litmus, and still more so than phenolpthalein,—becomes yellow again. It is then with reason, that Lescoeur* proposed replacing the old litmus test, to determine the neutrality of salts, by the following rule: "The term *neutral* will be reserved for the state of a neutrality such that, on one hand, the helianthin remains yellow, and on the other hand, the phenolphthalein remains colorless and the litmus red."

Polyvalent Bases and Polybasic Acids.—If a soluble hydroxide of a polyvalent metal be neutralized progressively by a monobasic acid, each equivalent of acid added liberates the same quantity of heat; thus with barium hydroxide, a bivalent base, we have:

$$Ba(OH)_2 + 1 \text{ eq. HCl liberates } +13.85 \text{ Calories}$$

$$Ba(OH)_2 + 2 \text{ eq. HCl liberates } +2 \times 13.85 \text{ Calories.}$$

It is different in the reverse process. If to one molecule of a polybasic acid there be added successively one, two, three, molecules of a monoacid base, we obtain, in general, very different quantities of heat at each addition (always decreasing, except with sulphuric and oxalic acids), so that each hydrogen of the acid appears to play a distinct rôle in neutralization, as is shown by the following table:

Neutralization by Na OH	Acid					
	HCl	H_2SO_4	H_3PO_4	$H_2C_2O_4$	H_2CO_3	H_3BO_3
1 equivalent	13.7 Cal.	14.7 Cal.	14.7 Cal.	13.8 Cal.	11.10 Cal.	11.56 Cal.
2 equivalents	.....	16.7 "	11.6 "	14.7 "	9.4 "	8.26 "
3 equivalents	.....	.....	7.3 "	.....	.....	negligible

It follows from this that the sulphuric and oxalic acids are clearly characterized as dibasic with helianthin or litmus, the end

*H. Lescoeur, *C. R.*, cxxiii, 811 (1896).

point being distinct when a trace of the alkali be added in excess of the two equivalents, while the phosphoric acid acts with helianthin like a monobasic acid (the red coloration disappearing when a little more alkali is added than the first equivalent) and with phenolphthalein like a dibasic acid (the pink coloration appearing after the second equivalent of alkali). For the same reasons, carbonic acid is characterized as monobasic in a very distinct manner by phenolphthalein, rather indistinctly by litmus, and not at all by helianthin.

In a general way, it is only monobasic acids and a few rare dibasic acids (sulphuric and oxalic acids) which can be titrated accurately by alkalies in the presence of colored indicators while soluble mineral bases are accurately titrated by acid solutions.

This difference in the rôle of the acid and basic properties of polyvalent compounds is only apparent. It depends simply upon the fact that all soluble polyvalent mineral bases are very strong—they are confined, in practice, to alkaline earth bases—and give consequently with strong acids neutral salts, which, in aqueous solution, do not present any appreciable trace of hydrolysis. Each molecule of a monobasic acid added to an aqueous solution of one molecule of these divalent bases is combined then *entirely* with the base, and the change in the color of the indicator can take place only when an excess of acid is added in excess of the two molecules. It is not the same with medium, strong or weak polybasic acids. We have seen (Chapter III., Section 1) that the salts of weak acids in solution are always more or less strongly hydrolyzed, even when these acids are combined with strong bases (like sodium borate for example), while producing an equilibrium represented by the general law:

$$\frac{C_{\text{free acid}} \times C_{\text{free base}}}{C_{\text{non-hydrolyzed salt dissolved}}} = k$$

The first portions of the alkali added combine then almost completely with the dissolved acid, and the last portions not at all, so that the preceding equality is satisfied. The change in the color of the indicator will then be produced in an intermediate stage, and generally in an indifferent manner, unless some acid salts of a certain stability may be formed (these considerations apply as well to the polybasic as to the monobasic acids).

If we knew some soluble salts of polyacids the bases of which are of medium strength or weak, they would give exactly the same

result in consequence of the hydrolysis of their salts in solution, furnishing in the preceding equation an appreciable value of k, while with barium hydroxide, for example, this value is clearly nil, and we would have decreasing liberations of heat, for each equivalent of monobasic acid added—consequently, titrations indefinite or impossible to accomplish as with weak polybasic bases. Polyacid salts of medium or weak organic bases are known, moreover, which give exactly this result. Such is the case of ethylenediamine, a diacid base, one molecule of which liberates +12.5 Calories with the first equivalent of HCl and +11.0 Calories with the second,* orthophenylenediamine, a diacid base, which liberates +7.0 Calories with the first HCl and +3.0 Calories with the second,† etc.

The inequality of strength of the different acid hydrogens of the same polybasic acid, and the divergence which is offered in this respect in volumetric titrations by the basic metallic compounds and polyvalent acids, are then only apparent anomalies, which are easily explained by the degree of hydrolysis of the corresponding salts in aqueous solution.

2. Gravimetric Methods by Double Decomposition

These methods are by far the most numerous in analytical chemistry, in which they form the larger part of the so-called *wet methods.* They require the previous knowledge of the peculiar properties of each insoluble or but slightly soluble salt used, and of its reciprocal actions with the soluble salts used as reagents, a study of which should be made in each particular case, based upon the principles which we have previously established. Already, in the course of the presentation of these principles, we have treated a rather large number of special cases taken as examples; we will complete them by the study of the general method of research and of the methods of separation by hydrogen sulphide and alkali sulphides, which constitute a necessary stage in almost all of the analyses of the metallic minerals.

Detection and Separation of Metals by Hydrogen Sulphide and Alkali Sulphides.—By means of hydrogen sulphide, we divide the metals, for practical purposes, into two large classes; metals precipitated by hydrogen sulphide in acid solution, and metals not separated under the same conditions.

* A. Colson and Darzens, *C. R.*, cxviii, 250 (1894).

† Vignon, *C. R.*, cix, 477 (1889).

The sulphides precipitated in acid solution are in their turn subdivided into two groups by the alkali sulphides which dissolve some (sulphides of metals with acid properties giving sulpho-salts) and do not dissolve others (sulphide of metals with basic properties).

The metals which are not precipitated by hydrogen sulphide in acid solution are likewise divided into two groups by the alkali sulphides which precipitate some (sulphides insoluble in water, but easily soluble in acids) and do not precipitate others (sulphides soluble in water).

This method is not at all general and could serve only for particular separations of the four groups of metals thus formed by means of these two reagents containing only unequal numbers of elements; but it happens that, by a quite fortuitous circumstance, these four groups each contain almost exactly the same number of metals, including only the most important elements, or those widely distributed in nature, which gives the maximum effect, useful in employing these two reagents:

Metals Precipitated by Hydrogen Sulphide in Acid Solution		Metals not Precipitated by Hydrogen Sulphide in Acid Solution	
Sulphides Soluble in Alkali Sulphides	Sulphides Insoluble in Alkali Sulphides	Metals Precipitated by Alkali Sulphides	Metals not Precipitated by Alkali Sulphides
Arsenic	Mercury	Zinc	Barium
Antimony	Silver	Nickel	Strontium
Tin	Copper	Iron	Calcium
Gold	Lead	Manganese	Magnesium
Platinum	Bismuth	Aluminium	Sodium
	Cadmium	Chromium	Potassium

Let us see now the conditions to be realized in order that this method should give certain results.

1. *Separation by H_2S into Two Classes.*—The precipitation of the metals from their salt solutions by H_2S is a reaction of equilibrium, limited by the redissolution of the sulphide in the acid of the salt set free. With some metals, the solubility of the sulphide in the strongest acids, medium dilute, is extremely slight, and the precipitation as complete as can be desired (arsenic, silver, mercury, copper). However, all the precipitated metallic sulphides are capable of being redissolved in concentrated strong acid, hydrochloric acid, for example, and it is necessary not to exceed a certain degree of acidity

for a practically complete precipitation of the metals, lead, bismuth, cadmium, antimony and tin. Moreover, the properties of metallic sulphides vary in a continuous manner from one metal to the other, and certain metals form the transitions from one class to the next. It is in this manner that the sulphide of cadmium redissolves in rather dilute HCl and that zinc sulphide precipitates only partially from a liquid containing a small proportion of this free acid. The action of H_2S upon $ZnSO_4$ limited by that of H_2SO_4 upon ZnS, was one of the first equilibria studied, as we have seen, and the equilibrium is represented by the law:

$$\frac{C^{i}_{ZnSO_4} \cdot C^{i'}_{H_2S}}{C^{i''}_{H_2SO_4}} = k,$$

k having a value equal on the average to 2.4 at ordinary temperature, according to the observations of W. Ostwald (see Chapter IV, Section 3). The precipitation may even become practically complete, starting from a neutral solution of $ZnSO_4$ if $C^{i}_{ZnSO_4}$ is reduced to an extremely small value, for the concentration of H_2SO_4 cannot, in any case, exceed that of $ZnSO_4$ at the beginning, and tends towards this definite final value. It is sufficient to increase the concentration of H_2S to a value still quite moderate in order that the precipitation should become complete in dilute solutions.

It is necessary then to add quite a large proportion of free strong acid in order that the zinc should not precipitate at all. On the other hand, the acidity must be rather slight in order that the lead and cadmium, whose coefficient k is not much larger than that of zinc, should be completely precipitated by H_2S. It is apparent then, that the separation of metals into two groups by H_2S is far from being strictly exact and that, even in order that it should be approximate, it is necessary to start with solutions of a carefully determined acidity.

A special property comes in, it is true, to aid greatly the realization of the desired conditions for a good separation; that is, the moderate solubility of hydrogen sulphide, 0.13 of a molecule of which saturates completely one liter of water at 15°. This is a relatively small concentration and it is because this amount cannot be exceeded in the ordinary conditions of analysis in which we operate at atmospheric pressure, that metals, like nickel and iron are not at all precipitated from a solution of the neutral chloride by

the prolonged passage of a current of hydrogen sulphide gas. The concentration of hydrochloric acid coming from double decomposition is still sufficient, even in very dilute solutions, to counterbalance the effect of H_2S at the maximum concentration, and thus no precipitate is produced; or, at least, a few drops of free acid suffice to completely prevent it. It will be noticed that, if the solubility of H_2S had been much greater or less, there would have been a displacement of the metals to the limit of each class; if less, the calcium would be in the third group; if greater, the zinc and perhaps the nickel might be in the second.

By observing the rule for adding to the *neutral* solution a tenth of concentrated hydrochloric acid, and of saturating the cold solution with H_2S, the separation into two groups is as exact as possible, but with the appearance of traces of zinc in the second group.

2. *Subdivision of the Two Classes into Four Groups by Alkali Sulphides.*—The first class alone is to be considered from the point of view of special precautions to be observed as the solubility or insolubility in water of the sulphides of the second class is very clearly defined. To subdivide the sulphides of the first class into soluble or insoluble sulphides in the alkali sulphides it is necessary to employ preferably the sulphide of sodium, which is less hydrolyzed than the sulphide of ammonium. The latter gives, in fact, a small proportion of free ammonium hydroxide, which acts upon certain metals, like copper, forming with ammonium soluble complexes and causing a little of the copper to pass into solution.

With arsenic, antimony and tin, the formation of sulpho-salts is immediate and the dissolution is rapid; for gold and especially for platinum, it is much slower and in this case the solution is difficult to accomplish, the acid function of platinum sulphide being but slightly marked. It is, moreover, a quite general rule, that the acid function of the elements of the same family diminishes in proportion as the atomic weight increases and inversely for the basic function; this can be verified in the series: N, P, As, Sb, Bi,—Li, Na, K, Rb,—Ca, Sr, Ba,—etc.* Platinum, which is related to the tin family, forms thus the transition of the sulphides with acid properties to sulphides with basic properties.

* From the recent investigations of C. Matignon (*C. R.*, cxlii, 276 (1906)), the oxides of the rare earths would be an exception to this rule. In the series La, Pr, Nd, Sa, the basic properties diminish as the atomic mass of the metallic element increases.

3. Methods Based on Hydrolysis

General Characteristics of these Methods.—Although the phenomena of hydrolysis are reversible, in certain cases, it happens that the decomposition giving a precipitate is sufficiently complete so that the precipitate can serve for the quantitative determination of the hydrolyzed salt; such is the case for bismuth, tin, titanium, aluminium, and ferric oxide.

We saw (Chapter III, Section 1), that the decomposition of salts by water presents, as do all double saline decompositions, very different speeds, according as the decomposition is *simple* (separation of the acid and base) or *complex* (formation of a basic salt). In the first case, it is immediate; in the second, which is the only one to be considered in methods of analysis based on hydrolysis, it requires a greater or less time to arrive at the state of true equilibrium, this delay depending on the nature of the bodies present, the temperature and the dilution.

For the hydrolysis of the chloride of bismuth, the limit is reached in the cold in a few minutes. On the contrary, the hydrolytic decomposition of the salts of tin, titanium, iron is very slow in the cold and the limit is reached only at the end of a considerable period of time; as this decomposition absorbs heat, consequently it is accelerated greatly by bringing the solutions to boiling. For salts slightly hydrolyzed, such as acetates of the protoxide metals, the acceleration of hydrolysis is not very perceptible on increasing the temperature, and this unequal rapidity allows the separation of iron from the metals of the magnesium series.

For the chloride of bismuth and of antimony, whose decomposition liberates heat, it is, on the contrary, by cooling the solution as much as possible that the most rapid and complete decomposition is obtained.

The acid of the salt to be hydrolyzed can be chosen in a manner so that the limit of decomposition is the maximum. Hence, by prolonged boiling, the sulphates precipitate SnO_2 and TiO_2 much more completely than the chlorides; for bismuth the precipitate is much more complete with the chloride than with the nitrate. These differences come from the fact that in the equation of equilibrium of the reaction: $C^{ni}C'^{n'i'} = kC''^{n''i''}C'''^{n'''i'''}$, the coefficient k varies from one salt to another, and it is necessary to choose the acid of the salt for which the transformation is the most complete (k minimum). In

general, the hydrolysis for the same acid is more complete in proportion as the acid is weaker (liberating less heat in combining with the oxide); therefore the precipitation of Fe_2O_3, SnO_2, TiO_2 by hydrolysis is more rapid and complete, if we start from a hydrochloric or sulphuric acid solution, adding an alkali acetate in excess, which has for effect the combining of the strong acid with the alkali and of changing Fe_2O_3, SnO_2 and TiO_2 to the acetates which are incomparably more hydrolyzed than the chlorides or sulphates.

Dilution always results in the increase of hydrolysis. If we take, for example, the decomposition of the chloride of bismuth:

$$BiCl_3 + H_2O \leftrightarrow BiOCl + 2HCl,$$

the law which controls the equilibrium (assuming the coefficients i as equal), BiOCl being insoluble is then:

$$C_{BiCl_3} \cdot C_{H_2O} = k\, C^2_{HCl}$$

Now C^2_{HCl} has a maximum finite value which corresponds to the complete decomposition of $BiCl_3$; k has equally a finite value, very small, moreover, and their product consequently keeps a finite value. If, then, we increase indefinitely C_{H_2O}, the value of C_{BiCl_3} (concentration of the bismuth chloride remaining in solution) will decrease indefinitely and will take as small a value as one wishes. In practice, we cannot give to C_{H_2O} a value greater than that which corresponds to a two-liter flask containing a maximum of about one gram of metal in the form of chloride, but that suffices to obtain a complete precipitation of bismuth chloride for which the coefficient k is very small. For antimony chloride, the coefficient k has a very much greater value, so that, although in appearance the two chlorides are precipitated, the one as easily as the other, by water, we cannot obtain for antimony, with the usual reagents, a precipitation complete enough for this method to be applicable to separations of antimony.

We see then, after all, that the study of the conditions to be observed in the methods based on hydrolysis ought to include:

1. The choice of the acid of the salt giving the maximum hydrolytic dissociation.

2. The examination of the stability of all the salts formed by the chosen acid with all the oxides present in the solution.

3. The determination of the thermal sign (heat absorbed or evolved) of hydrolysis showing at what temperature it is proper to experiment.

We will take as an example of the application of these principles the so-called *"acetate method,"* frequently used for the separation of iron and aluminium and protoxides of metals of the magnesium series (Mg, Zn, Mn, Ni, Cu), which are frequently associated in the oxide minerals of iron or of zinc and in the metallic sulphides.

"The Acetate Method."—The protoxides of the metals enumerated above, are bases of average strength which give with acetic acid and its homologues, salts stable enough to be practically not decomposed by boiling for a few minutes. On the contrary, the acetates of iron and aluminium are decomposed in a warm solution in a few seconds and deposit a mixture of the oxides and the subacetates insoluble in water. The method of operation, based upon this difference of stability of acetates, is the following:

We start generally with a hydrochloric acid solution of the oxides. After having oxidized the iron and almost neutralized the solution, we add an excess of alkali acetate sufficient to transform all of these acetates and to have no longer any free acid except acetic acid; then boil a quarter of an hour—aluminium and iron precipitate, completely carrying with them very small quantities of other metals. Filter and wash with boiling water, redissolve the precipitate with hydrochloric acid, and a second similar treatment, repeated again, if necessary, gives an excellent separation.

We have then to examine at first if, among the homologues of acetic acid and of similar strength, acetic acid is the best suited by its properties for this method of separation, because other acids, such as formic and succinic acids have also been proposed for the application of this method.

The choice of the acid ought to be made according to the heat of neutralization of the same dissolved base, sodium hydroxide for example, by the series of acids of analogous strength to acetic acid, and all those which give a higher heat of neutralization are to be rejected. Those which give a lower heat than acetic acid can produce a more complete precipitation of iron; but one should ascertain whether the difference of speeds of hydrolysis of protoxide salts of this acid and of the salt of iron remains sufficient so that the separation is quantitative. In fact, it is acetic acid which is best, for its heat of neutralization by sodium hydroxide (13.3 Calories) is less

than that of formic acid (13.4 Calories) and the other acids of the same series, which gives 13.5 Calories to 14.0 Calories; it is also weaker than that of benzoic acid (13.7 Calories) and of dibasic succinic acid, which gives 13.6 Calories with the first equivalent of sodium hydroxide. There is, then, no advantage in replacing the acetic acid by formic or succinic acids with the object of making the precipitation of iron more complete.*

In the series of mineral acids (non-reducing, which is necessary in order to leave the iron in its maximum state of oxidation) there no longer exist any acids giving with the oxides under consideration soluble salts whose heat of formation is below that of the corresponding acetates.

As to the choice of the alkali salt of acetic acid to be employed, one might wonder if it is not preferable to use ammonium acetate instead of sodium acetate. Ammonium acetate has the advantage, it is true, of introducing into the solutions a salt which is readily eliminated by ignition, but it is much more hydrolyzed than sodium acetate (7.60 per cent of ammonium acetates dissociated against 0.14 per cent of sodium acetate according to the researches of Debbits†); accordingly the solutions of ammonium acetate lose ammonia on boiling and become rapidly acid, and in conjunction with the appreciable hydrolysis of NH_4Cl, can give in case of too prolonged boiling, a degree of acidity sufficient to prevent complete precipitation of the iron. It is then preferable, save under conditions peculiar to each definite case, to employ sodium acetate.

We have in the second place, to study the stability of the acetates of the magnesium series at different temperatures, and the heat of dilution, in order to determine what are the metals which best lend themselves to separation by the acetate method.

In a sealed vessel, at a temperature of 175°, all the acetates of the magnesium group are decomposed with the formation of free acetic acid and the oxides of the metal (Riban, *Encyclopédie* de

*F. Schulze (*Chem. Centralblatt,* 1861, cited by Fresenius, p. 147, of the 6th French edition), advises sodium formate instead of the acetate, because, according to him, the precipitate of basic ferric formate is denser and easier to wash than the acetate. The latter appears sufficiently dense in operating with a rather large excess of alkali acetate and the advantage of the formate does not seem important to us. (Fresenius, Cohn, *Quantitative Chemical Analysis,* Vol. I, p. 197.—*Editors' Note.*)

† Debbits, *Bull. Soc. Chem.,* Paris (2) xviii, 490 (1872), and (2) xx, 258 (1873).

Frémy). This action of heat shows that, in the acetate method, it is necessary to carefully avoid heating directly the walls of the vessel not moistened by the liquid and which can reach thus a rather high temperature, with danger of producing, as I have shown, deposits of basic acetate or of oxides of zinc, nickel, etc., at the expense of the solution wetting the flask.

For solutions at ordinary pressure, we can divide the acetates into three groups:

1. Those which practically are decomposed neither cold nor hot; these are the alkali acetates (with the exception of ammonium acetate, which above 55° gives manifest signs of dissociation) and the acetates of the alkaline earths and of magnesium.

2. The acetates which decompose *slowly* cold or hot: these are the acetates of the ferrous iron family (magnesium) and copper. The acetate of zinc in dilute solution, which has been best studied in this respect,* and which can be considered as the type of these acetates, finally becomes turbid in the cold, losing acetic acid and depositing a small quantity of basic acetate (about one tenth in a year); hot, the same phenomena is produced more rapidly. But if we take care to prevent all loss of acetic acid, the solution remains clear, and treated with potassium hydroxide when cold, it liberates exactly the same quantity of heat, 5.40 Calories, as before heating. There are produced then here only perfectly reversible phenomena and nothing similar to what we are going to see in the case of ferric acetate.

It is sufficient, moreover, to leave a slight excess of free acetic acid in the dilute solutions of the acetates of this group, so as to compensate for the loss by evaporation during the heating, to avoid any precipitation of basic acetate.

3. Acetates which decompose slowly in the cold and rapidly when hot; these are the acetates of ferric iron, of aluminium and of chromium. The manner in which they decompose is, moreover, very different, according as it is a question of a solution of pure acétate (obtained by double decomposition between equivalent quantities of lead acetate and the sulphate of the metal) or of a solution mixed with another metallic salt (sodium sulphate, sodium acetate, etc.).

Ferric acetate is the one whose stability has been most completely studied by Péan de Sainte-Gilles, Berthelot, etc. A fresh

* M. Berthelot, *Méch. Chim.*, Vol II, p. 314.

solution of ferric acetate causes a veritable equilibrium between free acetic acid, a basic acetate and the non-hydrolyzed acid, but, in time, the liberated iron oxide experiences an irreversible transformation, while still remaining in pseudo-solution, and loses the property of combining with the acetic acid with which it co-exists: this is what is shown by the calorimetric measurements made by Berthelot* upon ferric acetate.

A fresh solution (one equivalent in two liters) treated with potassium hydroxide (one equivalent in two liters) liberates 8.87 Calories and gives still the same result three weeks afterwards. At the end of two months, the heat liberated amounts to 10.39 Calories, and at the end of eighteen months to 12.81 Calories, a figure almost equal to the heat of neutralization of the acetic acid and potassium hydroxide (13.3 Calories), which shows that the dissociation of ferric acetate has increased gradually until it is almost complete. The ferric oxide remains in colloidal solution, and is precipitated by salts of the metals. With a greater dilution the dissociation is accomplished more rapidly; in ten liters of water, the mixture liberates 12.82 Calories at the end of three weeks.

In a hot solution, the dissociation is almost complete instantly. The fresh solution, which in the cold liberates 8.87 Calories, with potassium hydroxide, raised to 100° for some minutes, then brought back to the ordinary temperature, remains clear, but treated immediately with potassium hydroxide, it liberates 12.72 Calories. The acetic acid and ferric oxide are then almost completely separated and, in fact, if we add to the solution sodium sulphate or acetate, the ferric hydroxide precipitates. However, if we keep the solution for several days, there is a progressive recombination of a little acetic acid and ferric hydroxide, for the potassium hydroxide liberates 12.56 Calories at the end of four days, and 12.13 Calories at the end of eighteen. But, here this recombination ceases, almost all of the ferric hydroxide having passed into the irreversible colloidal state, insoluble in acetic acid and in dilute sulphuric acid but still soluble in hydrochloric acid. This insolubility of the ferric hydroxide thus precipitated in an acetic acid solution shows that it can be initially acidified by this acid, on the condition that it contains an excess of sodium acetate or sulphate which accelerates and renders complete the transformation of ferric hydroxide into a complex insoluble in acetic acid, precipitating it in proportion to the transformation of the

* *Loc. cit.*, p. 297.

ferric acetate into acetic acid and ferric hydroxide in pseudo-solution.

The rôle of acetates of the alkalies added to the initial hydrochloric acid solution of the hydroxides is double; it produces hydrolysis by the transformation of the acetates, and it precipitates the colloidal ferric hydroxide, which, without the excess of alkali salt would remain in pseudo-solution and could not be separated from the other metals.

Aluminium acetate presents properties identical to those of ferric acetate; its solutions may be heated to 100° without becoming cloudy if they are pure, but the slightest trace of foreign salts precipitates them according to the early observations of Gay-Lussac. With chromium acetate, the hydrolysis is less complete and the acetic acid always redissolves a little hydroxide. One should then not recommend the acetate method in the presence of chromium salts, unless the latter have been previously transformed into alkali chromates.

The effect of the dilution has been studied, to our knowledge, only for ferric acetate and zinc acetate; for the first it absorbs —0.56 Calories when we dilute it from two to twelve liters, for the second, on the contrary, it liberates +0.01 Calories (Berthelot). This fact is particularly favorable to the acetate method, since, from the principle of the opposition of action and reaction, an elevation of temperature should render the hydrolysis of the ferric acetate more complete and that of zinc acetate less complete. It shows equally that it is best to filter while boiling and to wash with hot water, instead of operating in the cold. It is shown in fact that, if we let the liquids cool considerably before filtering, the filtrate carries with it a little iron and aluminium which can be precipitated by boiling.

Résumé: From this theoretical discussion it follows that the conditions to be realized in order to obtain the best possible results by the acetate method are:

1. Start with a hydrochloric acid solution, neutralize almost exactly with sodium carbonate, then add a rather large excess of sodium acetate, acidify slightly with acetic acid (the weight of the acetate being at least twenty times larger than that of the iron and aluminium to be precipitated).

2. Then boil about a quarter of an hour, without exceeding noticeably this period, to avoid the precipitation of the ferrous salts

(too prolonged boiling would also have the drawback of making the precipitate too fine and then it would pass too easily through the filter).

3. Filter the boiling liquid and wash the precipitate with boiling water containing a little sodium acetate, to prevent as much as possible the re-solution of the basic acetates.

4. To repeat the precipitation a second, or even, if necessary, a third time, redissolving each time the precipitate upon the filter with boiling dilute hydrochloric acid. This is done to obtain a more exact separation, the colloidal nature of the precipitate causing it to carry down with it by absorption a part of the salts in solution.

These deductions from the theory are exactly confirmed by practice in the analysis of minerals containing iron, zinc, etc.

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